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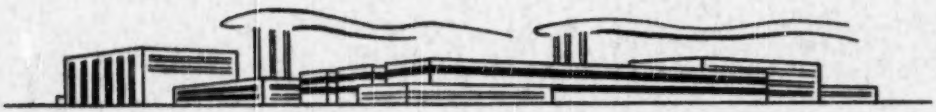

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TEXTILE RESEARCH JOURNAL

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The Role of the Electric Double Layer in the Sorption of Acids and Dyes by Wool

P. Alexander * and J. A. Kitchener †

THE LITERATURE concerning the combination of textile fibers with acids and dyes shows that, although a considerable amount of reliable data are available, the subject is in a confused state: numerous apparent discrepancies exist and no clear explanation has been given for the wide variety of observed effects. It is the purpose of this paper to show that the whole range of the phenomena concerned can be satisfactorily accounted for in terms of accepted concepts of the structure of electrical double layers. The argument will be developed with reference to wool, but it will be a simple matter to extend it to other fibers.

Structure of the Wool Fiber

Modern optical and electron-microscopic work [30] has proved that wool has a complex morphological structure comprising exterior scales, an underlying thin membrane [14], interior elongated cortical cells, and microfibrils connected together by amorphous material. Although the scales obstruct the entry of dyes [27] and contain a somewhat greater proportion of cystine [8], they show electrophoretic behavior identical with that of the cortical cells [20]. For the present purpose, it is not necessary to take the morphological structure into account and the wet fiber may be regarded simply as an infinite homogeneous cylinder having molecular channels of relatively large dimensions, the existence of which is amply proved by the ability of large molecules to penetrate into the fiber.

The polypeptide chains with their variety of side chains, having *inter alia* $-NH_2$ and $-COOH$ groups, are held in position by hydrogen bonds [3] and disulfide links. There can be no doubt from the clear findings of Speakman [24] on the mechanical properties of wool as a function of pH that at the isoelectric point of the wool (defined by zero electrokinetic potential) the amino and carboxyl groups exist largely in the zwitterion condition, $-NH_3^+ \ldots {}^-OOC-$. The fact that addition of neutral salts has no influence on the extensibility [25] proves that the two groups are very close together, forming the so-called "salt link," which may be pictured as a dipole. It is, perhaps, more than a coincidence of nature that the amino and carboxyl groups are present in equal numbers—approximately 0.8–0.9 equivalents per kg. of dry wool.

X-ray diffraction patterns of wool fibers show that their degree of crystallinity is appreciable [2].

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As yet, these patterns have not been interpreted completely and the proportion of crystalline to amorphous material is not known.

The Double Layer in Wool

The sorption of acids or dyes by fibers is entirely analogous to the adsorption of electrolytes by inorganic colloids, which has been thoroughly studied by many workers, notably those of the Kruyt school. Although all ions are attracted to some extent to all surfaces, if only by ion-induced dipole forces, Verwey and Kruyt [31] have shown that it is convenient to classify ions in relation to a given surface as either (*a*) "leading" or "potential-determining" or (*b*) indifferent. The former are those which can be strongly bound to the surface, usually owing to primary valency forces, whereas the latter have no specific affinity and are merely attracted electrostatically as gegenions in the diffuse double layer. This distinction between ions is not fundamental, being solely a matter of relative affinities, but it is convenient when the differences between the affinities of the two types are very great, as is often the case.

Adsorption of the electrolyte is supposedly due almost entirely to the affinity of the potential-determining ions. The high affinity of these ions is offset by the increasing charge built up by the ions on the surface, and when the other ions have no affinity the adsorption isotherm closely approximates the logarithmic form familiar for the charging of a metal electrode.

According to the Gouy-Chapman theory, the gegenions, which have no specific affinity for the surface, set up a diffuse double layer which extends into the solution. The thickness of this diffuse layer is of great importance for the theory of textile dyeing. Approximate solutions have been obtained for the fall of potential across the double layer for various cases [32]. For textile fibers with diameters greater than 10μ the flat-plate theory would appear to be the nearest approximation. The "thickness" $\frac{1}{\kappa}$ of a flat double layer varies as

$$\frac{1}{(\text{concentration})^{\frac{1}{2}} \times (\text{valency of gegenion})},$$

a typical value being 100 Å. for a $10^{-2}N$ uni-univalent salt. Figure 1 shows the calculated ionic distribution in the neighborhood of a charged surface, according to Verwey and Overbeeck [32].

The above picture of the double layer can be applied directly to wool. The only simple ion which shows true chemical affinity for a protein is the proton, which is, therefore, generally the sole potential-determining ion. It can be bound only to specific basic groups (chiefly $-NH_2$ and COO^-), but owing to the range of amino acids present in any one protein there is a range of affinities (*i.e.*, acid strengths) which gives overlapping titration curves. It has been found possible to correlate the observed titration curves of soluble proteins with their amino-acid content [5].

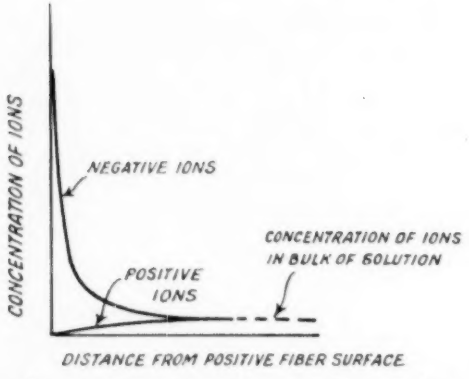

FIG. 1. *Ionic distribution near a charged fiber surface [32].*

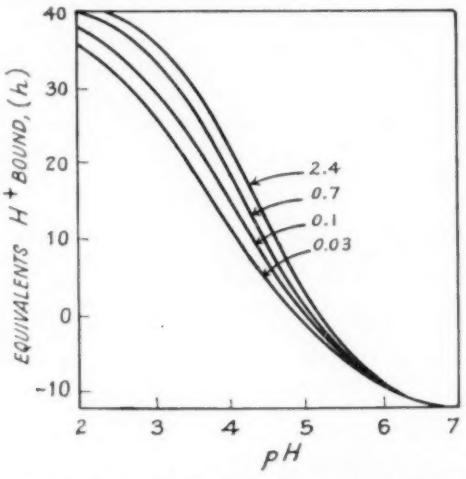

FIG. 2. *Effect of salt on the titration curve of egg albumin at four different ionic strengths [4].*

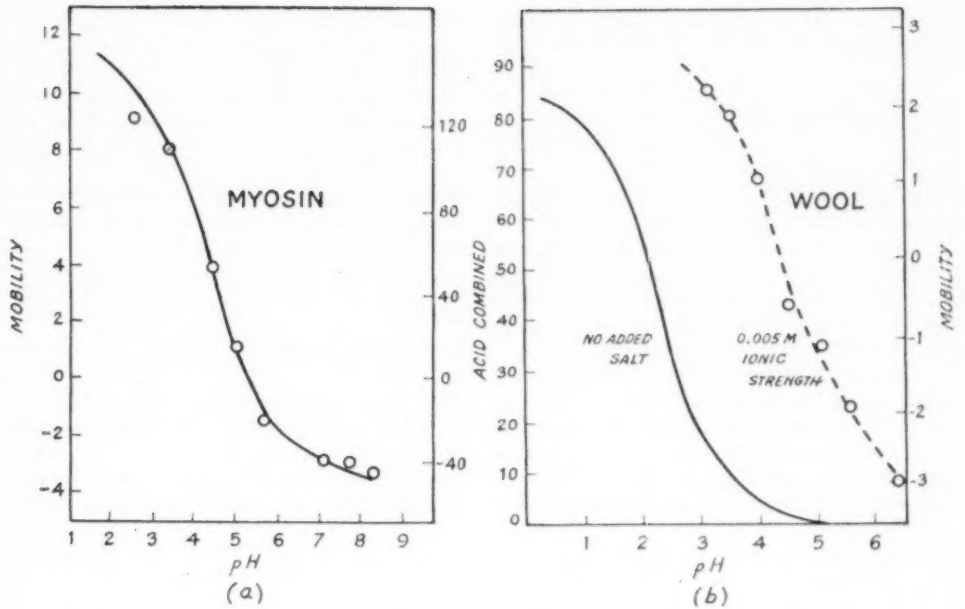

FIG. 3. *Comparison between the effect of pH on electrokinetic mobility and acid-combination curves for soluble and insoluble proteins.* (*a*) *Myosin* [7]. (*b*) *Wool* [20, 28]. (*Points: electrokinetic; continuous curves: acid combination.*)

Anions and cations other than hydrogen cannot combine covalently with proteins and are therefore "indifferent" unless their molecular weight is high. In that case, as will be shown, they develop a semi-specific affinity for the surface, owing to van der Waals forces. This type of affinity is responsible for the phenomenon of dyeing and, unfortunately, it is not yet possible to treat it quantitatively for the complicated molecules and surfaces involved. When present to a small degree, anion affinity may be pictured on the Stern double-layer model—the gegenions being held close to the charged surface, thus partly neutralizing its effect. Such anions, because of their greater affinity, replace the simple ion (*e.g.*, the chloride) present in acid wool, and it is by this anion exchange in the double layer that acid dyeing proceeds. No dye is taken up until the wool has bound some acid and, with it, gegenions, which can be replaced by dye ions. Certain ions have so great an affinity that they may even become potential-determining; sorption can then occur quite independently of hydrogen-ion combination. This is the mechanism by which "neutral dyeing" of wool and "direct dyeing" of cotton take place.

Difference Between Soluble and Insoluble Proteins

If the protein is considered as a simple colloidal particle, salts which contain no potential-determining ion should have only the effect of condensing a pre-existing diffuse double layer without influencing the charge on the surface, and this has proved to be a satisfactory basis for explaining the influence of salts on the stability of colloids. Consequently, the quantity of acid bound by a protein at a given pH (*i.e.*, fixed activity of the potential-determining ion) would be expected, at first sight, to be independent of added electrolytes. Experiment shows, however, that the addition of salts assists the binding of acid and bases of both soluble and insoluble proteins, although the effect is much greater with the latter. In the case of soluble proteins, the large molecules, carrying many charges, have activity coefficients which can be very different from

unity and the effect of salts can be calculated approximately by means of a Debye-Huckel treatment [5].

The titration curves for insoluble proteins (*e.g.*, wool and silk) show that the binding of protons by $-NH_2$ and $-COO^-$ groups occurs in two distinct regions which are well separated by an almost "isoelectric region" (see Figure 4), whereas in the case of soluble proteins these regions merge into one continuous curve which passes straight through the isoelectric point with scarcely an inflexion (see Figures 2 and 3(a)). The addition of salt closes up the two parts of the fibrous-protein titration curve until it approaches that of a soluble protein.

The difference in behavior of soluble and fibrous proteins toward salts can best be seen from the quantitative relations. Cannan *et al.* [4] have shown that for a soluble protein—*e.g.*, egg albumin—the salt displacement of pH (ΔpH) for a given number of protons bound, (h), is well represented by the relationship

$$\Delta\text{pH} = \alpha h + \beta,$$

where α is a function only of the ionic strength and β is a constant. In contrast, Gilbert and Rideal [9] have shown that for wool $\frac{\theta}{1-\theta} = K[H^+][Cl^-]$, where θ is the fraction of the available sites occupied by protons. Hence at a given value of θ and different chloride concentrations

$$[H_1^+][Cl_1^-] = [H_2^+][Cl_2^-];$$

i.e.,

$$\Delta\text{pH} = \log \frac{[Cl_2^-]}{[Cl_1^-]},$$

which is an expression of quite a different character from that for egg albumin. In the case of egg albumin, the salt shift is therefore linear with the amount of acid bound, whereas in the case of wool it is independent of acid binding (Figures 2 and 4).

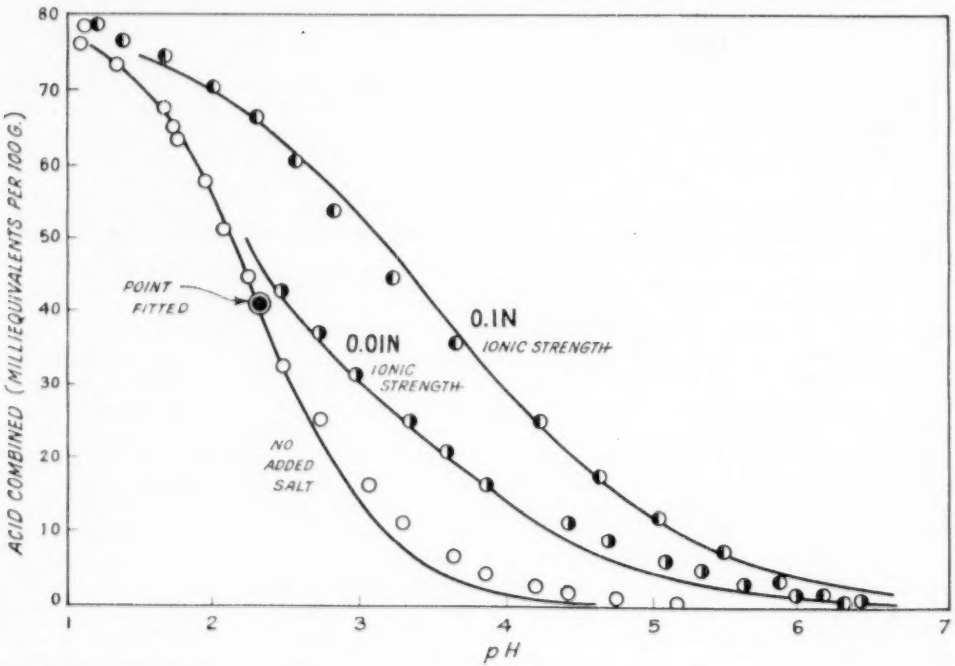

FIG. 4. *Theoretical and experimental acid-binding curves at different ionic strengths for wool. Points experimental [28]; curves calculated from theory of Gilbert and Rideal [9], fitted at one point only and corrected for activity coefficient of chloride ion.*

Further information concerning this problem may be obtained from measurements of electrokinetic properties. These give information only on the nature of the diffuse double layer and can in the main be accounted for by the simple model of the latter. In the case of many pure soluble proteins, electrophoretic mobility curves and titration curves are superimposable (Figure 3(a)) and both are in complete accord with the picture of a spherical molecule with all the charges residing on the surface, the *zeta*-potential being proportional to the charge. This evidence and the ability of proteins to form unimolecular films at water/air and water/oil interfaces indicate clearly that single protein molecules are sufficiently flexible to be able to orient their polar and non-polar groups in opposite directions. Thus, the diameter of globular protein molecules in solution is of the order of 30 Å., whereas the thickness of a monolayer on water is only 7.5 Å.

Insoluble fibrous proteins cannot behave in this way and marked differences between the mobility of their microscopic particles and their titration curves are observed (Figure 3(b)). The isoelectric point of wool determined electrophoretically is at pH 4.4, whereas its zero acid binding point is at about pH 6. It is interesting to note in this connection that cold drawing (*i.e.*, increasing crystallinity) of nylon modifies its electrokinetic properties, which suggests that polar groups are forced into less accessible positions without, of course, changing the titration curves materially [12].

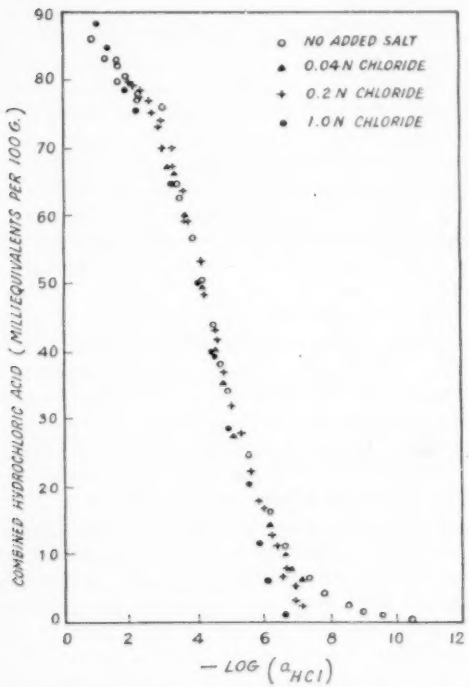

FIG. 5. *Applicability of law of mass action to the combination of HCl with wool at different ionic strengths.*

Attempts to find the isoionic pH on the titration curve by selection of the point at which addition of KCl does not influence the acid binding appear to be without theoretical foundation, owing to the influence of anion affinity. According to the data of Steinhardt and Harris [29], such a point would be at pH 6.3, whereas consideration of tensile strength and minimum swelling would indicate an isoelectric region at pH 5 to 8. This difficulty of fixing the isoionic point does not arise with soluble proteins, which can be recrystallized until they are substantially free from extraneous ions. Thus, pure β-lactoglobulin when dissolved in water gives a pH identical with that of the isoelectric point fixed electrophoretically [4]. This pH is not the one at which added salt has zero effect.

Model for Fibrous Proteins

The simple double-layer model is adequate for soluble proteins in which polar groups are on the outside, but must be modified for insoluble proteins, which form fibers in which obviously only a small proportion of the polar groups can possibly be on the outside. It is therefore proposed to distinguish between "outside" and "inside" sorption sites; the former control the electrokinetic properties, whereas the latter have no very long-distance influence, but, by their numerical preponderance, determine most of the titration curve.

In view of the porous structure of a swollen fiber, it is necessary to define precisely what is meant by "outside" and "inside." The value obviously depends upon the size of the measuring unit employed and for the present purpose the important factor is the effective range of the interionic forces. Since this range is modified by the concentration of free electrolyte, it cannot be taken as constant and will be considered to be of the same order as the thickness of a diffuse double layer under the given conditions.

There must exist a series of complete equipotential contours in the double layer surrounding the fiber. Of these, the locus of the "center of gravity" of the double layer is typical. According to the thickness, $\left(\frac{1}{\kappa}\right)$, of this line, it will follow either the coarse or the fine structure of this surface. Similarly, an equipotential line can be imagined for the maximum value of the potential at the surface and this forms a convenient definition for the boundary between outside and inside.

When potential-determining charges on a protein are separated by distances greater than the thickness of the double layer—*e.g.*, in the neighborhood of the isoelectric point and in the presence of much indifferent salt (*i.e.*, salt having no affinity for the protein)—the distinction between "outside" and "inside" would disappear and the fiber would behave like a soluble protein. That this actually occurs is demonstrated by Figure 5, where it is seen that the correction for acid binding of fibrous (*i.e.*, "inside") protein due to a salt does not apply for small acid binding (see page 210). Under most circumstances, however, the thickness of the double layer is greater than or of the same order as the mean distance between potentially charged sites, which is of the order of 10 Å. for wool. Near the isoelectric point, when only 1% of the total possible sites in wool are charged, the separation is of the order of 30 Å., whereas the the thickness of the layer $\left(\frac{1}{\kappa}\right)$ in the presence of 0.1*N* neutral salt is only 10 Å. and the fiber becomes freely permeable to electrolytes.

Combination of Wool with Acids

At the isoelectric point, supposed at first to be identical with the isoionic point, the amino and carboxyl groups, assumed to be equal in number, exist largely as $-NH_3^+$ and $-COO^-$, although because of the overlap of the two parts of the titration curves there will be a small proportion of $-NH_2$ and $-COOH$ groups. In the isoelectric condition there is no *net* charge either "outside" or "inside" the fiber, and hence no electric double layer, because both sets of ions are held on fixed points. The mean electrical potential through the fiber is zero and there are only local potential fluctuations due to the salt-link dipoles. There may be potential effects due to oriented dipoles at the surface (*i.e.*, similar to the surface potential of an air/water interface), but in the absence of any quantitative data these will be neglected in the present discussion.

On the addition of a little hydrochloric acid to such a system, protons will combine with $-COO^-$ groups, thus converting dipoles into positive charges which build up an increasing potential on the fiber. At the same time, a diffuse double layer of chloride ions will be created which, because of the low ionic strength, will extend far into the solution.

As the electrophoretic mobility (see Figure 3(b)) tends to become constant at pH values (after pH 3.5) at which only a fraction of the total acid is bound, it appears that the outside combines with acid before the inside. The preferential sorption of protons on the outside seems probable from electrical considerations, for the most stable distribution would be reached with the charges separated as widely as possible and the behavior would be somewhat similar to that of an electronic conductor where all the charges are situated at the surface.

As more acid is added, a distribution of positive charges is set up as the protons begin to combine with the inside carboxyl groups. The charge thus produced on the fiber repels additional protons, and if no gegenions enter the fiber more acid can be bound only by greatly increasing the concentration of acid. Such a charging process requires a logarithmic increase of concentration to produce equal increments of sorption; hence the acid binding by this mechanism should be linear with pH, which is found to be the case for most proteins, including wool, for a small region in the neighborhood of the isoelectric point.

However, when the acid concentration has been increased to about 100 times that at the isoelectric point, a much more extensive sorption process than that due to the logarithmic law begins to take place—namely, *the simultaneous entry of protons and gegenions into the inside of the fiber*. Near the isoelectric point this is of negligible importance, since the anion has no affinity for the fiber, and the entry of two particles is less probable than that of one.

The new sorption process requires entry of equal numbers of protons and anions and it is therefore controlled by both ions equally. The electrical work of introducing the two oppositely charged ions cancels out, since they finally come to regions of the same electrical potential,* and therefore this sorp-

* The "inside" is not a completely equipotential space and the variations of potential are important in the dyeing of fibers, but the fluctuations cancel out and the mean potential

tion mechanism is independent of the charge or potential of the outside electric double layer.

This concept is implicit in the theory of Gilbert and Rideal [9] for the acid binding of wool.† Their assumption of an unknown potential, ψ, inside the fiber, although not constant, gave essentially the correct result owing to the cancellation of ψ when equivalent numbers of opposite charges are held by the fiber. Gilbert and Rideal made the important contribution of showing that the shape of the titration curve can be largely predicted by taking account of the fact that there are only a limited number of salt links available for combination with protons. The combined ions may be regarded as occupying separate sites, since the protons combine covalently with the $-COO^-$ groups, while the chloride ions are held loosely in the neighborhood of the $-NH_3^+$ groups by Coulomb attraction. The $-COO^-$ groups are all supposed to have the same acid strength, but this is true only to a first approximation. The Gilbert and Rideal treatment is essentially equivalent to an application of two Langmuir adsorption isotherms for two sets of sites the relationship for which can be derived very simply.

The net reaction is described by the equation

$$(H^+ + Cl^-)_s \rightleftharpoons (H^+ + Cl^-)_f,$$

where subscript s is the aqueous solution and f is the fiber phase. At equilibrium, the chemical potential (μ) of hydrogen chloride is the same in the two phases, and since

$$\mu = \mu_0 + RT \log_e a,$$

where a is the activity,

$$\frac{a_f}{a_s} = K.$$

In solution, $a_s = (a_{H^+} \times a_{Cl^-})_s \doteq [H^+]_s[Cl^-]_s$.

The activity of a Langmuir adsorbate is given by $\frac{\theta}{1-\theta}$, where θ is the fraction of sites occupied. In the present problem θ is the same for the two ions. Therefore:

$$a_f = (a_{H^+} \times a_{Cl^-})_f = \left(\frac{\theta_H}{1-\theta_H}\right)\left(\frac{\theta_{Cl}}{1-\theta_{Cl}}\right) = \left(\frac{\theta_{HCl}}{1-\theta_{HCl}}\right)^2,$$

where θ_{HCl} is the fraction of salt links which have taken up HCl. Hence the titration curve should be given by

$$\left(\frac{\theta_{HCl}}{1-\theta_{HCl}}\right)^2 = K[H^+]_s[Cl^-]_s.$$

Therefore:

$$\log_{10}\frac{\theta}{1-\theta} = \tfrac{1}{2}\log_{10} K - \tfrac{1}{2}\,pH + \tfrac{1}{2}\log_{10}[Cl]_s$$
$$= \tfrac{1}{2}\log_{10} K - pH \text{ for pure HCl.}$$

If the chloride ion had no affinity for the wool, the pK of the carboxyl group would be equal to $-\log K$. The pK for HCl on wool = 2 × (pH at half neutralization with pure HCl) = 4.4.

That this theory gives good agreement with experiment over a large portion of the titration curve can be seen from Figure 4. A better fit can hardly be expected from the recognized over-simplification of assuming that only one strength of carboxyl group is present. No allowance is made for the interaction of charged NH_3^+ groups with neighboring salt links. The failure to fit the experimental results near the isoelectric point is to be expected in view of the difference in the titration curve for the outside of the fiber, and the overlap with the $-NH_2$ titration curve, which has not been considered. This overlap is, of course, most marked at high ionic strengths and will change the shape of the experimental curve, which is the sum of the two theoretical curves for the combination of protons with NH_2 and COO^-.

At high acidities a point of difficulty in fitting experimental values to theory is the correction for the amount of acid which is imbibed by the fiber but is not combined with the salt links. Steinhardt and Harris, whose experimental data have been used by all of the other authors, have assumed that there is non-solvent water present to the extent of 30% on the weight of the wool. Peters and Speakman [18] have made a different correction by employing the Donnan membrane theory and, as a result, give a somewhat higher maximum acid combining power.

Effect of Neutral Salts on Acid Binding

The considerable influence which neutral salts have in the combination of acid or dyes with fibers is readily understood on the basis of the model discussed above. Two effects must be distinguished—namely, that on the dimensions of the double layer

of the "inside" is that of the highest potential contour in the double layer surrounding the fiber.

† The acid-combining theory of Steinhardt and Harris [29], which also successfully accounts for the experimental results, is fully discussed by Gilbert and Rideal [9].

and that on the partition of acid between the solution and the inside of the fiber.

The condensation of the Gouy diffuse layer due to increased ionic strength, which, at low-charge densities, may even reduce $\frac{1}{\kappa}$ to a value less than that of the mean distance between the charged sites, will facilitate the approach and penetration of cations (*e.g.*, protons) into the capillaries, and hence, when diffusion inside the fiber is rate-controlling, increase the rate of sorption. Reduction in the width of the double layer will also increase the binding of acid by the "outside" groups owing to the Debye-Huckel activity effect. The method of calculation of Linderstrøm-Lang [5] for soluble proteins could be applied to the problem. However, the proportion of groups "outside" is usually so small compared with the number "inside" that it would affect only the part of the titration curve close to the isoionic point.

By far the most important effect of neutral salt is that due to the common ion effect. This arises because the greater part of acid binding involves the simultaneous entry of anion and proton into the fiber even though only the latter is strongly bound. Consequently, acid-binding curves at different ionic strengths, which are widely different when plotted on a pH axis (see Figure 4), should become superimposable when plotted against the product of the activity of the proton and the anion. That this is, in fact, the case is shown in Figure 5, where the data of Steinhardt and Harris are plotted against $-\log_{10} a_{HCl}$.

$$-\log_{10} a_{HCl} = \text{pH} - \log_{10} ([\text{Cl}]_s \times f_{KCl}),$$

where f_{KCl} = mean activity coefficient of KCl.

It should be emphasized that this superimposition involves no structural assumption; we did not have to postulate any kind of model for deriving this expression.

The curves are not accurately superimposable at low acid binding and high ionic concentration and the mass-action treatment over-corrects for the chloride ion effect because the titration of the "outside" groups becomes important in this region, and these "outside" groups, behaving like soluble protein, are not so greatly affected by added salt as the "inside" groups are.

At very high ionic concentrations the difference between "inside" and "outside" disappears over a large part of the titration curve and the whole fiber behaves like a soluble protein.

Anion Affinity

Anions do not enter fibers only as gegenions but are capable of behaving as leading or potential-determining ions, bringing with them cations as gegenions. The following lines of evidence establish this point.

1. *Electrokinetic Evidence.*—Although some simple salts such as potassium chloride have very little influence on the electrokinetic properties of surfaces other than closing up the double layer, salts with larger anions exhibit pronounced effects of a semi-specific kind. For example [34], sodium acetate lowers the pH of the isoelectric point of egg albumin [23], and Sookne and Harris [20] obtained large shifts for wool in phthalate buffers.

Lowering of the electrokinetic potential by such salts might possibly be ascribed to sorption of anions on top of protons in the manner postulated in the Stern theory of the double layer (a smaller proportion of the gegenions being left free in the diffuse part of the double layer), but the shift of the isoelectric point, when there are no gegenions, cannot be thus explained. If phthalate is added to isoelectric wool, direct sorption of the phthalate ion renders the surface negative and therefore more protons are required (*i.e.*, a lower pH) to restore it to the isoelectric condition. The existence of an isoelectric point for cotton [21]—which contains only acidic groups and yet becomes positive below pH 2.5—proves that there must be sorption of cations by non-Coulombic forces.

2. *Acid-Binding Evidence.*—Overwhelming evidence of anion affinity is provided by Steinhardt, Fugitt, and Harris [28] and others on the titration of wool with acids of increasing molecular weight. The amount bound at a given pH increases with the molecular size and complexity of the anion, the titration curve being displaced an approximately constant amount to higher pH's. High anion affinity therefore has the same effect as increasing the active mass of an anion of low affinity.

3. *Supra-Stoichiometric Acid Binding.*—Wool has an approximately constant maximum acid-combining capacity for different acids of about 0.8–0.9 milliequivalents/gram, but considerably more than this quantity of organic acids of high molecular weight can be taken up at low pH's. There is a sharp rise in sorption with such acids [28] at low pH's which might be entirely physical in nature. However, Speakman and Elliott [26] have maintained that this is not so, and that the binding is

strictly stoichiometric, the excess being due either to ionization of the NH groups or to hydrolysis of the fiber with the liberation of more amino groups. Skinner and Vickerstaff [22] observed the sorption of as much as 1.3 milliequivalents/gram of Disulphine Blue V and 2.1 milliequivalents/gram of Carbolan Blue onto wool at pH 1.2, but they supposed that these results could be explained by postulating that each amino group sorbed one molecule of the dibasic dyes. Such an explanation cannot explain the supra-stoichiometry of Polar Yellow R [10] and the obvious explanation of direct anion affinity seems much more plausible. It is further supported by the fact that 0.18 and 0.29 milliequivalent of Disulphine Blue V and Carbolan Blue, respectively, are taken up at pH 6.1, which is close to the point of zero acid binding for simple dyes.

Finally, many "neutral dyeing" acid wool dyes are taken up at neutrality even by cotton. This dyeing is undeniably due to anion affinity and there is no reason why such affinity cannot also contribute to the uptake of acid dyes with large anions by wool.

4. *Nature of Anion Affinity.*—For small ions, anion affinity is, of course, very small compared with proton affinity due to $-COO^-$ groups. For example [23], the displacement of isoelectric point produced by 0.1*N* sodium acetate is counteracted by addition of $5 \times 10^{-6}N$ hydrogen ions. The tendency for a proton to combine is, therefore, roughly 2×10^4 times greater than for sorption of an acetate ion. Nevertheless, anion affinity increases so greatly with ionic size that for dye ions it becomes comparable with the proton affinity.

There is no chemical valency to account for anion affinity, and it is clearly brought about by physical forces of a non-Coulombic type—*i.e.*, van der Waals forces, including ion-dipole, dipole-dipole, and London dispersive forces, hydrogen bonding, and surface activity—resulting in the deposition on a less-polar interface such as the fiber surface [1]. The relative importance of these factors will depend upon the nature of the fiber, and the order of affinities of a series of dyes will thus not be the same on different fibers.

Dyeing Equilibria

1. *Pure Dye Acid.*—In addition to the extensive series of measurements by Steinhardt, Fugitt, and Harris [28] already mentioned, which include the dye acids, the sorption of pure dye acids by wool has been studied by Speakman and Elliott [26] and by Lemin and Vickerstaff [15]. The last paper appears to show that the Gilbert and Rideal theory gives approximate agreement with experiment, and these authors have used it to calculate values for the "affinity" ($\Delta\mu^0$) of the dye for the wool, which is defined by the equation

$$\Delta\mu^0 = -RT \log_e K,$$

where K is the equilibrium constant for the dyeing equilibrium

$$(H^+ + D^-)_{soln.} \rightleftharpoons (H^+ + D^-)_{fiber},$$

that is, $K = \dfrac{(a_{H^+}a_{D^-})_{fiber}}{(a_{H^+}a_{D^-})_{soln.}}$. $\Delta\mu^0$ is the free energy of transfer—one molecule of H^+D^- from solution to fiber when the activities in both phases are unity. The units of activity are in solution gram-molecules per liter and for a component i on the fiber $\dfrac{\theta_i}{1 - \theta_i}$. It is readily seen that rough constancy of the final value of $\Delta\mu^0$ for a series of measurements does not constitute a sensitive test for the validity of the theory employed. Thus, even for the simple dye Orange II [reference 15; see Table 1] the value for K when derived from $\Delta\mu^0$ is far from constant; these values are, nevertheless, better than those obtained with more complex dyes. The deviations arise from three causes: (1) the theory considers dye anions only as gegenions (although with some "affinity") and takes no account of the possible sorption of the dye anions as the leading ions where they would not behave like a Langmuir adsorbate; (2) there may be interaction between the large neighboring sorbed dye molecules, as the sites are not far apart; and (3) the assumption that activity coefficients are unity is certain to be erroneous even at low concentrations for large dye anions.

2. *Dye Salt with Added Acid and/or Salt.*—Practical dyeing is generally carried out in the presence of mineral acid and neutral salt (*e.g.*, sodium sulfate). The first increases and the second decreases the equilibrium uptake of the dye (see Figure 6). The hydrogen ions supplied by the mineral acid combine with the $-COO^-$ groups and all the anions present (*i.e.*, dye anion and anion from acid and salt such as sulfate) *compete* for the position in the double layer. Elöd [6] showed that the mineral acid combines very rapidly and the simple anions (*e.g.*, chloride or sulfate) go into the fiber first with

the protons; the dye anions subsequently replace them because of their greater affinity. The fiber behaves like an anion-exchanger of constant capacity if sufficient acid is present to combine with all the carboxyl groups. Addition of neutral salt decreases the equilibrium sorption of dye and results in easier leveling by maintaining a higher concentration of dye in solution by mass-action competition. Neale's explanation [17] that the addition of salt decreases the electrical attraction between the positively charged wool fiber and the dye anion is misleading. The wool fiber already has its sheath of gegenions and there is no net electrical attraction; the dye enters the fiber because of its greater affinity due to secondary forces and thus replaces the other anion. The process of dyeing involves no special electrical attraction but is a simple ion exchange which can be formulated thus:

$$(H^+ + Cl^-)_{soln.} \rightleftharpoons (H^+ + Cl^-)_{fiber};$$

$$(H^+ + Cl^-)_{fiber} + D^-_{soln.} \rightleftharpoons (H^+ + D^-)_{fiber} + Cl^-_{soln.};$$

therefore:

$$K = \frac{(a_{Cl^-})_{soln.} \times (a_{D^-})_{fiber}}{(a_{D^-})_{soln.} \times (a_{Cl^-})_{fiber}}.$$

Kitchener and Kressman [13] and others have shown that ion exchange follows the classical law of mass action and that a constant, K, is obtained if concentrations are used for activities both in solution and in the solid. This does not mean that the activity coefficients in the solid and in the solution are the same but only that the ratio of the activity coefficients of different ions in the solid and in solution is approximately a constant, since activities in both solution and solid occur on both sides of the equation; this simple concept holds well in practice. The dyeing equilibrium of simple acid dyes in the presence of excess mineral acid is thus readily treated and the effect of neutral salts is predictable to a good approximation.

3. Basic Dyes.—The present authors do not know of any detailed measurements of equilibrium between wool and simple basic dyes. By analogy, however, it can be predicted that one dye cation would be bound for every proton ***removed*** from the salt links by increasing pH.

Neutral salts would facilitate the breaking of salt links by common ion effect but would reduce dye adsorption by competition (this time, of cations). The basic dyes which have occasionally been used on wool (*e.g.*, Methylene Blue, Eosin, and the Rhodamines) owe their dyeing properties to high cation affinity rather than to simple base binding, and they are generally applied from neutral or feebly acid solution rather than from alkaline solution. It is the salt rather than the base which is taken up because the dye cation acts as a potential-determining ion, whereas the chloride ion is drawn in as a gegenion. The mechanism is therefore exactly parallel with that for anionic neutral dyes.

4. Neutral Dyeing.—In neutral dyeing the dye anion is the leading ion and the sodium ion enters the fiber as the gegenion; hence addition of sodium chloride promotes the adsorption of dye, and this effect can be thermodynamically treated as the common ion effect of the sodium ion. The case is exactly parallel with acid binding where the chloride acts as a common ion. The effect of salt is also immediately obvious from the double-layer picture. The wool is negatively charged at neutrality, and this charge is increased as soon as a few dye anions are sorbed and an extensive double layer is set up on the outside of the fiber. Large additions of neutral salt reduce the thickness of the double layer —although they do not directly affect its charge— and permit dye anions to approach closer to the surface, where they come within range of the secondary physical forces leading to adsorption. When the thickness of the double layer becomes less than the distance between the adsorbed or bound ions, the fiber becomes freely permeable to electrolytes, including the dye anion. Thus, when dyeing is carried out in the presence of mineral acids, salts reduce the equilibrium sorption owing to anion competition, whereas in neutral dyeing salts increase the proportion of dye adsorbed at equilibrium. This point is illustrated in Figure 6, where the sorption of Orange II at pH 2 and 6 is shown to take place both in the presence and in the absence of salt. Not much of the dye is sorbed at neutrality because the anion affinity of this simple dye is not great, although it is sufficient to replace sulfate and chloride in the double layer.

Experiment shows that the sorption isotherm for a neutral dye cannot be represented by a Langmuir curve. Nor would this be expected, since, in this case, the fiber can obviously not be treated as a limited number of equal energy sites but must be considered as a large number of varying energy sites. Halsey and Taylor [11] have shown that under these conditions the adsorption isotherm is

correctly represented by the Freundlich formula. The data on the sorption of direct dyes on wool are scanty and confused because of the simultaneous uptake of dye by anion exchange [22], but it may be expected that the general behavior will be similar to that of direct dyes on cotton, which has been more extensively studied. Here it is well known that the Freundlich adsorption isotherm is generally applicable. Although this isotherm lacks the simple theoretical basis offered by the Langmuir isotherm, it could certainly be conveniently adopted as a ready means of characterizing the dyeing behavior of different dyes. The dyeing equilibrium could be formulated as follows (for a univalent dye, for simplicity):

$$(Na^+ + Dy^-)_{soln.} \rightleftharpoons (Na^+ + Dy^-)_{fiber};$$

$$\frac{[Na^+]_f \cdot [Dy^-]_f}{[Na^+]_s \cdot [Dy^-]_s} = K.$$

Experimentally, from a solution of constant excess salt concentration the equilibrium is found to obey an isotherm of the form

$$[Dy^-]_f = A[Dy^-]_s^m,$$

where A and m are constants for the particular dye and fiber. Since $[Na^+]_f \doteq [Dy^-]_f$, substitution gives

$$\frac{A[Dy^-]_s^m}{[Na^+]_s \cdot [Dy^-]_s} = K.$$

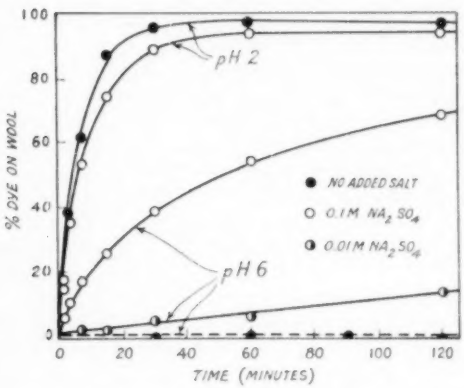

Fig. 6. *The effect of salts in increasing uptake of Orange II at pH 6 and decreasing dye uptake at pH 2. (Temperature 25°C; well agitated bath, ½% dye on weight of wool.)*

It follows that log $[Dy^-]_f$ should also be linear with log $[salt]_s$ for dye baths with fixed dye concentration, a result which has been observed.

This treatment would appear to offer a simple method of tabulating the characteristics of different direct dyes, since the constants A, m, and K, once determined, would give the dye uptake from a bath of any composition. That a rigorous attack on the problem from the molecular theory is hopelessly difficult at the present time is shown by the attempt of Willis, Warwicker, Standing, and Urquhart [33], who were forced to simplify the problem to such an extent that their final conclusions were equivalent to a formal thermodynamic treatment.

More recently, Peters and Vickerstaff [19] have put forward another theory in which the adsorption of dye is pictured as a partition of the dye between the external solution and an internal solution of constant volume v. The value of v must be taken as the water of imbibition, or else be obtained empirically by fitting; internal ion concentrations are calculated by the Donnan membrane theory and the activity of adsorbed dye ions is assumed to be proportional to their amount. It is clear from the preceding discussion that the kind of very rough agreement found with any quasi-thermodynamic treatment of this sort [16] does not constitute proof of the validity of the theory, since many other postulates would have led to a similar rough agreement.

Indeed, it does not seem likely that any treatment of direct dyeing is likely to be entirely satisfactory until a great deal more is known of the internal structure of fibers and the semi-specific forces at work. Furthermore, there is a great need for basic research on the activity coefficients of dyestuffs in solution in the presence of added salts, since it is certain that these coefficients will be abnormal, and nothing but the crudest fit would possibly be expected for any theory employing concentrations instead of activities.

Summary

It is shown that the various phenomena associated with the sorption of acids and dyes by wool can be readily understood in terms of the recognized properties of an electrical double layer.

Dyes are taken up either as gegenions to the charged groupings within the fiber or as leading ions bound by non-Coulombic forces and carrying inorganic gegenions with them into the fiber.

The effect of salts and acids on dyeing equilibria can be formulated by means of the law of mass action used in conjunction with the appropriate adsorption isotherm. It is emphasized that activity-coefficient data for dye solutions are needed before further progress can be made.

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The Impact of Raindrops on Fabrics

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Abstract

A study has been made of the pressure-time relationships existing during the impact of waterdrops on fabric surfaces. The impact was recorded by a high-speed motion-picture camera. Calculations of the pressure exerted by the waterdrop, the depth of penetration, and the manner in which the waterdrop deforms during impact are given. The theory described gives important principles that could be used for the design of water-repellent fabrics. If the fabric surface is plain the pores must be small so that the pressure required to force water through them will be high. An alternative or complementary method is to make the fabric surface highly compressible (*e.g.*, raised fabrics); the pressure exerted by the raindrops will be much smaller than in the former case. The requirements for the testing of water-repellent fabrics are examined in the light of the theoretical and experimental results reported herein.

DURING RECENT YEARS raincoats of water-repellent, air-permeable fabrics have been widely used, and great efforts have been made to make them as effective against rain as are the water-tight (or waterproof) fabrics. Because the latter are not permeable to water vapor and air, they are less comfortable.

The effectiveness of water-repellent fabrics depends upon both the fabric structure and the treatment used to impart water-repellency. Two opinions about suitable fabric structures have been reported in the literature. Baxter and Cassie [1, 3] have treated theoretically the conditions for wetting water-repellent fabrics. They state that a suitable fabric structure should have the fibers as homogeneously distributed as possible and should be highly porous, thus giving high apparent contact angles and unstable water films between the fibers. On the other hand, it has been stated that a very close fabric structure, withstanding a high hydrostatic pressure [5] or giving low values of air-permeability [8], is most suitable for raincoat fabrics.

In working with test methods for water-repellent fabrics, this question arises: How great a pressure will a falling raindrop exert when striking a fabric? One estimate of this pressure is reported in the literature [7], but it is too rough for forming any conclusions.

Because the course of the impact of a falling waterdrop on a solid foundation is of both practical and theoretical interest, we have studied it with the aid of high-speed motion pictures and have made an approximate calculation of the pressure as a function of time. An exact calculation is expected to be extremely complicated, if at all possible.

Experimental Investigation

The change of the shape of the drop during the course of impact was studied with the aid of a high-speed motion-picture camera of the rotating-mirror type, manufactured by Zeiss. The camera was made for 16-mm. film and was operated at a highest speed of 6,000 pictures per sec. At this speed the size of the pictures was 9×3.5 mm. The light from a dim glowing lamp, steered by a tuning fork, was projected on the film, giving rise to 1,000 marks per sec. It was therefore possible to determine the time that had elapsed between the pictures on the film.

The impact was studied both on ordinary water-repellent cotton fabric (plain weave) and on a film of cellulose acetate. During the experiment the samples were fastened in an embroidery frame. The drops were formed in a capillary, leaving at a rate of 90 drops per min. The radius of the drops was 2.3 mm. and their falling height 1.85 m. Under these conditions the velocity of the drops at the time of impact was about 4.6 m. per sec. (determined from the photographs). The photographic film had a length of 30 m., which enabled two consecutive drops to be photographed on one film.

The first drop fell on the dry sample. The second drop fell on the same place—therefore, on a wet surface. The drops struck the surface at right angles, and the impact was photographed at nearly right angles to the falling direction (Figure 1).

Figure 2 shows the course of impact of waterdrops on dry, water-repellent cotton fabric. The time that elapsed between two consecutive pictures was about 2×10^{-4} sec. Figure 3 shows the impact on dry acetate film. The film was cross-ruled, each square being 5×5 mm. These squares can be seen on the pictures and used as a scale. The time between two consecutive pictures was 2.0×10^{-4} sec. (scale, 1:1).

The pictures reveal some interesting relationships. During impact the upper part of the drop retains its spherical shape while the lower part is pressed outwards as a continuous film. Furthermore, the upper part has about the same velocity as immediately before the impact. This means that the change in the state of motion of the lower part of the drop was not propagated to the upper part during the first course of the impact. The shivering of the drop into droplets occurs much later, when the whole drop has become flat. The second drop, which falls on a wet fabric, loses its spherical shape more quickly because the contact angle is lower.

From the calculations of the pressure we get an expression for the deflection of the material during the impact as a function of time. This deflection can also be determined experimentally. A small strip of paper was fastened to the lower side of the acetate film, and the film was fixed in the frame. The waterdrop was adjusted to fall just above the strip (see Figure 4). The movement of the strip during the impact in relation to a fixed scale was photographed with the camera described above. From the photographs the deflection could be measured as a function of the time. The result is given in connection with the mathematical treatment of the deflection.

Mathematical Treatment of Waterdrop Impact

Definition of Symbols

E = modulus of elasticity
g = acceleration of gravity
h = height of the deformed drop
p = pressure between the drop and the foundation
p_s = pressure required to force water through fabric
P = total force due to drop = $p \times$ area
r = radius of the drop
s = depth of penetration of water into fabric
t = time
u = distance of center of gravity of the drop from the surface of the foundation at time t

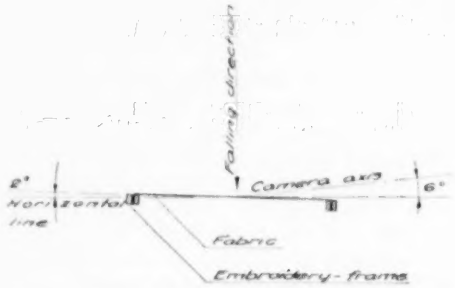

FIG. 1. *Diagram showing the arrangement used for photographing the course of impact of waterdrops on a fabric surface.*

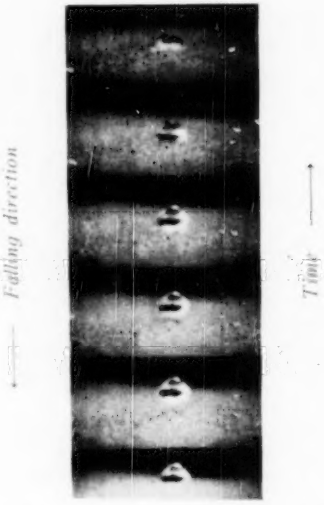

FIG. 2. *Photograph of impact of waterdrop on dry, water-repellent, plain-weave cotton fabric. (Time between consecutive pictures is approximately 2×10^{-4} sec.)*

v_0 = velocity of drop at beginning of the impact

w = deflection of the foundation at time t

$\dot{w}, \ddot{w}$ = first and second derivatives of w with respect to time

γ = mass of foundation per unit area

δ = fraction of the radius by which the drop is deformed at time t

$\dot{\delta}, \ddot{\delta}$ = first and second derivatives of δ with respect to time

μ = density of the drop (1 for water)

ν = Poisson's constant

ξ = distance between positions of center of gravity of the drop at $t = 0$ and $t = t$

$\dot{\xi}, \ddot{\xi}$ = first and second derivatives of ξ with respect to time

ρ = radius of the area of contact

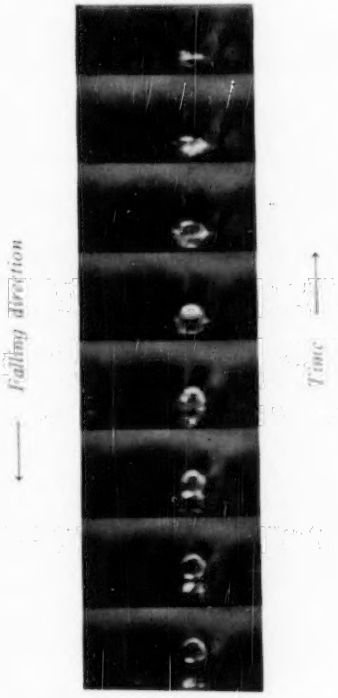

FIG. 3. *Photograph of impact of waterdrop on a dry film of cellulose acetate. (Time interval between consecutive pictures is* 2.0×10^{-4} *sec.)*

Impact on an Incompressible, Tensionless Membrane

During the course of impact a pressure arises between the drop and the foundation, the amount of which is a function of time. In order to calculate this pressure the following assumptions are made: (1) the foundation is assumed to be a tensionless membrane, thus influencing the course of impact only by its mass; (2) the membrane is hydrophobic, and thus the vertical component of the surface tension is small and can be neglected; (3) the drop does not penetrate into the foundation. (The surface tension and the state of motion within the drop determine the shape of the drop. An exact calculation of this shape is extremely complicated. This investigation is founded on the shape determined from the photographs. In this way the action of the surface tension is taken into account.) Figure 5 is a schematic drawing of the impact of a waterdrop, made on the basis of these assumptions; further discussion is given after the calculations.

Acceleration of the Deflection of the Foundation.— According to the above assumptions the membrane is deformed only below the surface of contact between the drop and the membrane. The acceleration of the deflection is given by equation (1), derived from the second law of motion:

$$\pi\rho^2\gamma\ddot{w} = P,$$

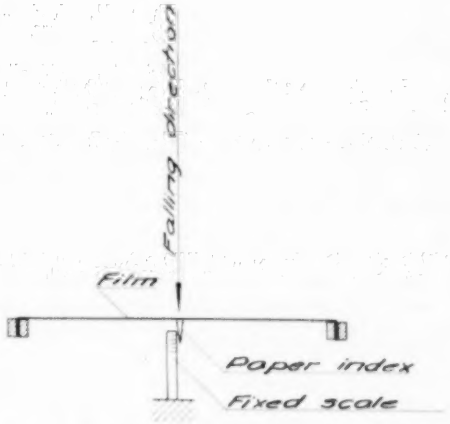

FIG. 4. *Diagram showing arrangement used for registering deflection of film resulting from the impact of a waterdrop.*

in which

$$\rho^2 = \delta rh = \delta r(2r - \delta r),$$

so that we obtain

$$\ddot{w} = \frac{P}{\pi r^2 \gamma \delta (2 - \delta)}. \tag{1}$$

Center of Gravity of the Deformed Drop.—Since we wish to apply the law of motion of the center of gravity, it is necessary to know the position of the center of gravity (C.G.) of the deformed drop. According to the photographs, the drop may be considered to consist of an upper spherical zone and a thin water layer on the membrane during the first part of the impact. If the water layer is very thin its C.G. is at the foundation and can be neglected in calculating u. From the value of the C.G. of a spherical zone and the volume of the zone the following equation can be deduced, giving the C.G. of the deformed drop, u:

$$\frac{4\pi r^3 \mu u}{3} = \frac{\pi r^3 (2 - \delta)^2 (1 + \delta) \mu \cdot r(2 - \delta)(2 + \delta)}{12(1 + \delta)};$$

$$u = r(2 - \delta)^3 (2 + \delta)/16. \tag{2}$$

The Differential Equation for δ.—By applying the law of motion of the center of gravity on the drop, equation (3) is obtained:

$$4\pi r^3 \mu \ddot{\xi}/3 = 4\pi r^3 \mu g/3 - P. \tag{3}$$

From equation (1) we get

$$P = \pi r^2 \gamma \delta (2 - \delta) \ddot{w}$$

and thus

$$\ddot{\xi} - g = -3\gamma\delta(2 - \delta)\ddot{w}/4r\mu. \tag{3a}$$

From the photographs in Figure 3 it can be seen that the upper part of the drop retains its state of motion during the first course of impact. The following equations are therefore valid:

$$v_0 t + gt^2/2 + h = w + 2r$$

or

$$w = v_0 t + gt^2/2 - \delta r. \tag{4}$$

According to the definitions, we get

$$w = u + \xi - r. \tag{4a}$$

By applying equations (2) and (4a) we get

$$-r + \xi + r(2 - \delta)^3 (2 + \delta)/16 = v_0 t - r\delta + gt^2/2. \tag{5}$$

By differentiating equations (4) and (5) two times we obtain

$$\ddot{w} = g - r\ddot{\delta} \tag{4b}$$

and

$$\ddot{\xi} = g + [3r\dot{\delta}^2(\delta/3 - 1)\ddot{\delta}]/4 - [3r(2 - \delta)\delta\dot{\delta}^2]/4. \tag{5a}$$

If $\ddot{\xi}$ and $\ddot{w}$ in equation (3a) are replaced by expressions in δ from equations (4b) and (5a) we get

$$\ddot{\delta}\left[\frac{\delta(1 - \delta/3)}{2 - \delta} + \frac{\gamma}{\mu r}\right] + \dot{\delta}^2 - \gamma g/\mu r^2 = 0. \tag{6}$$

During the first moments $\delta r \simeq v_0 t$ (*i.e.*, $\delta \simeq v_0/r$) and $\gamma g/\mu r^2$ will be small compared with $\dot{\delta}^2$ ($\gamma \simeq 0.03$ g. per sq. cm.; $v_0 \simeq 500$ cm. per sec.). The term $\gamma g/\mu r^2$ can therefore be neglected. When δ is less than 0.45, $\delta/3$ can be neglected in comparison with 1, and δ in comparison with 2, keeping the error below 10%. Equation (6) is then transformed into

$$\ddot{\delta}(\delta/2 + \gamma/\mu r) + \dot{\delta}^2 = 0. \tag{7}$$

Equation (7) can be easily solved. With the boundary conditions

$$t = 0 \begin{cases} \delta = 0 \\ \dot{\delta} = v_0/r \end{cases}$$

the following solution is obtained:

$$\delta = 2\gamma(\tau - 1)/\mu r, \tag{8a}$$

where

$$\tau = (1 + 3\mu v_0 t/2\gamma)^{\frac{1}{3}};$$

$$\dot{\delta} = v_0/r \times 1/\tau^2; \tag{8b}$$

$$\ddot{\delta} = -v_0^2 \mu/r\gamma \times 1/\tau^5. \tag{8c}$$

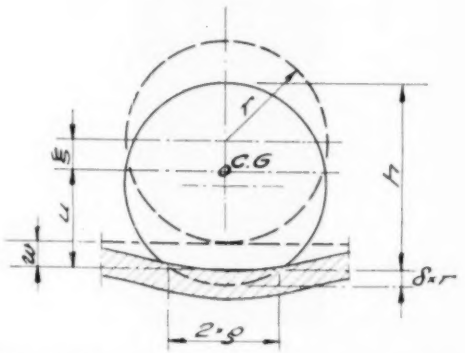

FIG. 5. *Schematic drawing of the waterdrop during the first part of the impact.*

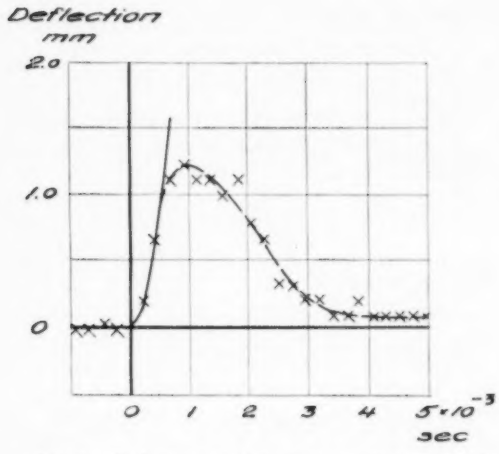

FIG. 6. *Deflection on impact of a cellulose acetate membrane, expressed as a function of time. (Experimentally determined points joined by dotted line; calculated points, by solid line.)*

Combining equations (1) and (4*b*), we obtain

$$g - r\ddot{\delta} = P/\pi r^2\gamma\delta(2 - \delta);$$

and by neglecting g and substituting equation (8*c*) for $\ddot{\delta}$,

$$P = \mu\pi r^2 v_0^2 \times \delta(2 - \delta)/\tau^5. \tag{9}$$

Equation (9) can be transformed with the aid of equation (8*a*):

$$P = 4\pi r\gamma v_0^2[1 - \gamma(\tau - 1)/\mu r] \times (\tau - 1)/\tau^5 \tag{10}$$

or approximately if $\gamma(\tau - 1)/\mu r$ is small compared with 1:

$$P \simeq 4\pi r\gamma v_0^2 \times (\tau - 1)/\tau^5. \tag{10a}$$

Equation (10) represents the final expression of P as a function of t, including only known quantities; it has a maximum and a minimum value. The minimum value occurs when $\delta > 0.5$ and is of no interest. The maximum value is determined in the usual way by differentiating equation (10):

$$\tau_{P_{max}} = 2\mu r[1 + 2\gamma/\mu r(+)(1 + \gamma/4\mu r + \gamma^2/4\mu^2 r^2)^{\frac{1}{2}}]/3\gamma \tag{11}$$

or approximately

$$\tau_{P_{max}} \simeq 5/4, \tag{11a}$$

corresponding to a maximum value of the approximate P-function given in equation (10*a*):

$$P_{max} \simeq 1.0 r\gamma v_0^2. \tag{11b}$$

TABLE I. DEFLECTION AS A FUNCTION OF TIME

$t \times 10^5$ sec.	w (calculated) (mm.)	w (experimentally determined) (mm.)
2.3	0.21	0.20
4.6	0.78	0.70
6.8	1.58	1.13

Pressure as a Function of Time.—The pressure, p, can be obtained if P is divided by the area of contact. Thus,

$$p = P/\pi r^2\delta(2 - \delta).$$

Substituting equation (9) for P, a simple relation for p is obtained:

$$p = \mu v_0^2/\tau^5. \tag{12}$$

Mean of the Pressure, p.—In order to get the mean of the pressure during the impact, we can make use of the following relationship:

$$p_{mean} = (1/t)\int_0^t p\,dt$$

which gives

$$p_{mean} = \tfrac{3}{2}\mu v_0^2\left[\frac{\tau + 1}{\tau^2(\tau^2 + \tau + 1)}\right]. \tag{13}$$

The mean of P can be obtained in the same manner.

Deflection of the Membrane, w.—According to equation (4) the deflection is given by

$$w = v_0 t + gt^2/2 - r\delta. \tag{4}$$

Substituting expression (8*a*) for δ we obtain

$$w = v_0 t + gt^2/2 - 2\gamma(\tau - 1)/\mu. \tag{14}$$

Table I and Figure 6 give the deflection as a function of time, both experimentally determined and calculated from equation (14). Because we have assumed the foundation to be tensionless for the deduction of equation (14) and since this condition is not fulfilled in the experiment, we can only get agreement between practice and theory during the first part of the deflection. For this reason the values obtained from equation (14) will exceed those obtained by experiment, which is the case. The conditions at the very beginning of the impact

on a compressible medium (see below) have no influence on the experimental results because the foundation in this case was a plain and very thin film.

The errors in the experimental results are due mainly to the following conditions. The drop must hit the film precisely above the paper strip. This could, however, be realized with sufficient accuracy. When determining γ, the weight of the paper strip was accounted for by adding it to the weight of the membrane. This procedure is only approximately accurate.

The experimental results show that at least under conditions similar to those existing during the experiment, the calculations give rather accurate values of the deflection in the beginning of the impact.

Impact on a Compressible Medium

Equation (12) was deduced assuming the foundation to be quite incompressible, thus giving a finite value of p at $t = 0$. In the beginning of the impact on a compressible surface, however, the compressibility of the foundation will dominate, and equation (12) will not be valid.

In order to describe these relationships we consider the foundation as an isotropic, semi-infinite, elastic medium, affected by a static pressure uniformly distributed over a circular surface with radius ρ. By applying the theory of Boussinesq [2], we derive the following expression for the maximum deflection:

$$w = 2p\rho(1 - \nu^2)/E, \tag{15}$$

where E = modulus of elasticity of the medium and ν = Poisson's constant. The other symbols have the same geometrical meaning as before, but they are not the same functions of the time. According to equation (4)

$$w = v_0 t + gt^2/2 - r\delta. \tag{4}$$

$gt^2/2$ can be neglected, and hence

$$w = v_0 t - r\delta.$$

From Figure 5:

$$\rho^2 = r^2\delta(2 - \delta).$$

Assuming equation (15) to be valid also under dynamic conditions and substituting in equation (15) for ρ and w, we obtain

$$p = \frac{E(v_0 t - r\delta)}{2r\sqrt{\delta(2 - \delta)}(1 - \nu^2)}. \tag{16}$$

If in equation (5*a*) we neglect g, $\delta/3$ in comparison with 1, and δ^2 in comparison with 2, the following expression is obtained:

$$\ddot{\xi} = -3r\dot{\delta}^2\delta/4 - 3r\delta\ddot{\delta}^2/2;$$

and from equation (3), neglecting the mass of the drop, we obtain

$$4\pi r^2\mu\xi/3 = -P.$$

Furthermore, $P = p\pi\rho^2$; hence,

$$p = \mu r^3\delta(\delta\ddot{\delta} + 2\dot{\delta}^2)/\rho^2.$$

Substituting expression (16) for p, we get

$$\delta\ddot{\delta} + 2\dot{\delta}^2 = \frac{E(v_0 t - r\delta)}{2^{\frac{1}{2}}\mu r^3\delta^{\frac{1}{2}}(1 - \nu^2)}. \tag{17}$$

Equation (17) can be written

$$\delta\ddot{\delta} + 2\dot{\delta}^2 = a(t - r\delta/v_0)/\delta^{\frac{1}{2}},$$

where

$$a = Ev_0/2^{\frac{1}{2}}\mu r^3(1 - \nu^2).$$

The differential equation (17) cannot be solved exactly, and it is necessary to use successive approximations. The following approximate expression is assumed, containing the two first terms in a power series for δ:

$$\delta = C_n t^n + C_m t^m + \cdots. \tag{18}$$

C_m and m are obtained after differentiation two times and introduction in equation (17). Since equation (17) is of interest only for small values of t, we can neglect terms of higher degrees than the two lowest ones. C_n and n were obtained, assuming the solution to be

$$\delta = C_n t^n.$$

Equation (18) can then be written

$$\delta = C_n t^{6/5}\left(1 - \frac{78C_n r}{227v_0} \times t^{1/5}\right), \tag{19}$$

where

$$C_n = (25a/78)^{2/5}.$$

δ must be determined from equation (19), and the pressure then calculated from equation (16). The latter equation contains Poisson's constant, ν. The magnitude of ν depends upon the elastic prop-

TABLE II. Pressure as a Function of Time, According to Equation (12)

$t \times 10^4$ sec.	τ	$p \times 10^{-3}$ dynes/sq. cm.
0	1	250
0.1	1.07	179
0.2	1.14	132
0.5	1.29	69
1.3	1.59	25
2.5	1.89	10
5.0	2.33	3.7
8.8	2.79	1.5

erties of the medium, but ν^2 can be neglected in comparison with 1 without too great an approximation.

Equation (12) gives the pressure if the foundation is quite incompressible and immediately yields to the drop, and equation (16) gives the pressure if the foundation yields to the impact only by a compression of the surface layers. When the resistance against motion depends upon both of the foundation properties, equations (12) and (16) form the upper limits of the acting pressure.

Numerical Calculation of the Pressure for Waterdrops of Different Radii

Numerical calculations were made for two different sizes of waterdrops: Drop 1, $r = 0.23$ cm., $v_0 = 500$ cm. per sec.; Drop 2, $r = 0.075$ cm., $v_0 = 500$ cm. per sec.

Drop 1 is of the same size as those used in these experiments and in the rain tester of the Swedish Institute for Textile Research [4]. Drop 2 corresponds to those occurring in natural rains of great intensity. The weight of the foundation per unit area, γ, is put equal to 0.032 g. per sq. cm., which corresponds to the weight of the cotton fabric used in the experiment.

When approximating equation (6) we determined the error to be less than 10%. Within these limits of error, equation (12) is valid until $\delta = 0.45$—*i.e.*, until the deformation of the drop is about half of its radius, or for Drop 1 until $t = 8.8 \times 10^{-4}$ sec., and for Drop 2 until $t = 1.3 \times 10^{-4}$ sec.

Table II gives the numerical values for the pressure at different times, calculated from equation (12). According to this relationship, the pressure is independent of the radius of the drop. The mean of p, calculated from equation (13) from $t = 0$ to $t = 1.3 \times 10^{-4}$ sec., is about 80 g. per sq. cm.

Equation (19) is more accurate for lower values of C and t. Since C depends upon E, this means that the equation is valid during different long periods for different moduli of elasticity. We have made the calculations for δ less than 0.5.

Table III gives the pressure as a function of time, according to equation (16). Figure 7 gives the pressure according to equations (12) and (16). The magnitude of E has a great influence on the acting pressure, which is limited upwards by equation (16) during the first part of the impact. Small values of E, implying a high compressibility of the surface layer of the foundation, give small values for the acting pressure. When E is of the order of magnitude of 2×10^3 g. per sq. cm. or higher, the decrease of the acting pressure, due to the local compression of the surface layers, will be of little practical importance.

According to equations (16) and (19), p is slightly dependent upon r, so that we get larger pressures for smaller radii.

The total force, P, acting on the surface is, of course, greater with the larger drops. Figure 8 gives P as a function of time, according to equation (10). For the first part of the impact, P can be obtained from expression (16) by multiplying p by the value for the area of contact, but since it is of less interest, we have not made any numerical calculations of this quantity.

TABLE III. Pressure as a Function of Time for Various Moduli of Elasticity (According to Equation (16))

$t \times 10^4$ sec.	$p \times 10^{-3}$ dynes/sq. cm. Radius of drop = 0.23 cm. $E = 2$ g./sq. cm.	$E = 2 \times 10$ g./sq. cm.	$E = 2 \times 10^2$ g./sq. cm.	$E = 2 \times 10^3$ g./sq. cm.	$p \times 10^{-3}$ dynes/sq. cm. Radius of drop = 0.075 cm. $E = 2$ g./sq. cm.	$E = 2 \times 10$ g./sq. cm.	$E = 2 \times 10^2$ g./sq. cm.	$E = 2 \times 10^3$ g./sq. cm.
0.1	0.5	3.1	17	79	0.8	4.8	26	110
0.5	1.0	5.7	31	127	1.5	8.9	46	180
1.0	1.3	7.5	39	156	2.0	12	60	235
5.0	2.4	14	74	—	4.0	—	—	—
10.0	3.3	20	—	—	—	—	—	—

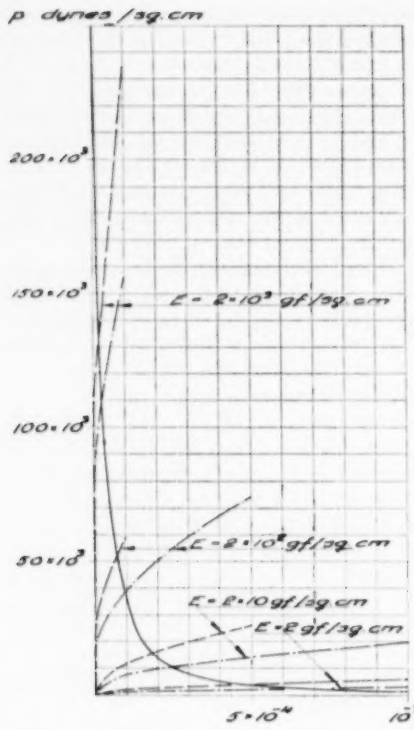

FIG. 7. *The pressure* p *from a waterdrop acting on the foundation or surface, expressed as a function of time. According to equations:* ———————— p *from equation (12);* — — — — — p *from equation (16), with* r = 0.075 *cm.;* — · — · — · p *from equation (16), with* r = 0.23 *cm.*

Discussion of the Assumptions

The assumptions for these calculations, given above, will be discussed further.

The foundation was assumed to be tensionless. This means that the course of impact will take a longer time than if the foundation were under tension. From Figure 2 we can see that the time necessary for $\delta = 0.5$ is about 4×10^{-4} sec., but according to the calculations the time is 8.8×10^{-4} sec. The difference depends upon the tension of the foundation during the experiment. It is to be noticed, however, that the two intervals of time are of the same order of magnitude. It would lead to extremely complicated expressions if the tension were taken into consideration in the calculations.

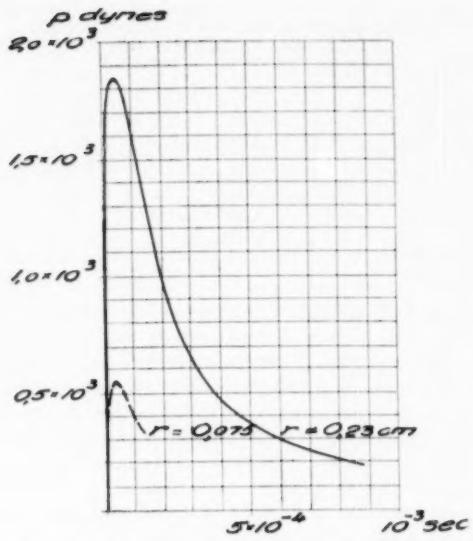

FIG. 8. *The force* P *acting on the foundation, expressed as a function of time.* ———————— p *from equation (10), with* r = 0.23 *cm.;* — — — — — p *from equation (10), with* r = 0.075 *cm.*

The numerical value of the pressure cannot be considered as exact, owing to the approximate character of the calculation, but the order of magnitude of the calculated pressure can be expected to be correct under the assumptions made. Also, the character of the influence of the different quantities on the pressure is probably valid.

Application of Theory and Data

The pressure relations during the impact of a raindrop against a fabric are important to the resistance against penetration of water into the fabric. Before applying the theoretical results to practical cases, we must first discuss the conditions for such application. One assumption in the calculation of the pressure was that the drop does not penetrate into the foundation. When the foundation is a fabric, this assumption is not met. However, a certain penetration will lower the acting pressure, and equations (12) and (16) will still form upper limits for the pressure. It is necessary that the diameter of the drop be large compared with the pores in the fabric if the theory is to be applicable.

From the high-speed motion pictures (Figures 2 and 3) it is seen that the course of impact is essentially the same whether the foundation is porous or

not. This shows that the mass penetrating is small compared with the mass of the drop for the cotton fabric in question, although the penetration may be rather deep (see below).

The calculation was restricted to the case of a drop striking a dry surface. If the surface is wet, we can expect to get a lower pressure, due to the damping effect of the water. As long as we make use of only the order of magnitude of the calculated pressure and the influence of the different quantities on the pressure, the theory developed above can be applied to the construction of water-repellent textiles.

A theoretical treatment of the conditions for wetting a porous fabric has been made by Baxter and Cassie [1]. These authors have shown that the penetration of hydrophobic fibers forming a fabric structure is due to the formation of stable water films between the fibers. A large fiber separation gives higher apparent contact angles and less stable films between the fibers, thus rendering the wetting more difficult.

In order to confirm this theory, Baxter and Cassie made the following experiment. Two fabrics of different constructions were tested, using both the hydrostatic pressure test and a shower test. One fabric was a proofed gabardine with a weight of 10 oz. per sq. yd. and the other, of the same weight, was made from open wool gauze with wool fibers lightly felted onto the gauze. The gabardine could stand a hydrostatic pressure exceeding 40 cm. (water column), whereas the gauze showed a breakdown pressure of 10 cm. When subjected to the shower of 3-in. rainfall per hr., the gabardine was penetrated within a few minutes, whereas the experimental fabric showed no penetration after a very long exposure. The result of the experiment, which can be explained by the theory of Baxter and Cassie and the pressure relationships during the impact, is treated below.

Depth of Penetration of the First Drop

When the apparent contact angle between the fabric and water is larger than 90°, a pressure is required to force water through the fabric. The magnitude of this pressure is dependent upon the advancing contact angle and the dimensions of the pores in the fabric. The water will pass into the pores between the warp and weft because penetration into yarns requires higher pressure [1]. If the apparent contact angle is less than 90°, no pressure will be required to force water into the fabric, because the water will be absorbed with the aid of the capillary forces of the fabric.

Considering a fabric with an apparent contact angle against water larger than 90°, a question of interest is: How deep will the first drop penetrate into the fabric?

Neglecting the difference in height and applying Bernoulli's law, we obtain

$$p_0 + \mu v^2/2 = p,$$

where v = velocity of the water, relative to the pore; p = pressure acting during the impact; p_0 = pressure required to force water through the fabric; and μ = density of water = 1.

The depth, s, of penetration during the time t can be written

$$s = \int_0^t v\,dt,$$

or

$$s = \int_0^t \sqrt{2(p - p_0)/\mu} \times dt.$$

We restrict ourselves to the calculation of the depth of penetration for a fabric with $E > 2 \times 10^3$ g. per sq. cm. (see below) and to which equation (12) can be applied.

By substituting equation (12) for p we obtain

$$s = (2^{\frac{1}{2}}\gamma/\mu v_0 \int_1^\tau \tau^2(v_0^2/\tau^5 - p_0/\mu)^{\frac{1}{2}}d\tau.$$

After expansion in a power series of the expression $(v_0^2/\tau^5 - p_0/\mu)^{\frac{1}{2}}$ and integration, we obtain

$$s = 2^{\frac{1}{2}}\gamma[2(\tau^{\frac{1}{2}} - 1) - p_0(\tau^{11/2} - 1)/11\mu v_0^2 - p_0^2(\tau^{21/2} - 1)/84\mu^2 v_0^4 - \cdots]/\mu.$$

If we assume that $p_0 = 25 \times 10^3$ dynes per sq. cm., $v_0 = 500$ cm. per sec., $\gamma = 0.032$ g. per sq. cm., and $t = 1.25 \times 10^{-4}$ sec. (which corresponds to $\tau = 1.58$), then $s = 0.035$ cm. This value is of the same order of magnitude as the value for the thickness of cotton fabrics used for raincoats. If $p_0 = 50 \times 10^3$ dynes per sq. cm. and $t = 0.6 \times 10^{-4}$ sec., we obtain $s = 0.013$ cm. When p becomes less than p_0, the penetration stops. Therefore, we must calculate the depth of penetration during

different long periods for different values of p_0 (see Figure 7).*

The penetration of water through a hydrophobic fabric may be thought to develop in the following manner. The first drop penetrates to a certain depth in the fabric. When afterwards the water surface contracts due to surface tension, the important point is whether a continuous water film is left between the fibers in the periphery of the yarns or not. If the fabric is thin and the acting pressure is large, a penetration of water through the fabric may occur although no film is formed between the fibers. But if the fabric is thick enough to withstand the pressure at the first impact and if continuous water films are not formed, no penetration of the fabric will occur during the continued action of raindrops. In most cases, however, there will be a water film between the fibers to a certain depth of the fabric, depending upon the magnitude of the pressure. The capillary forces will cause the water to be absorbed to this level. The pressure arising from the next impact will cause the water front to move deeper into the fabric, and so on, until it reaches the other surface of the fabric. When leakage has thus started, it will continue as long as water is transported to the surface of the fabric.

Influence of the Modulus of Elasticity of the Surface Layer

In order to get a numerical value of p from equation (16) we must know E, the modulus of elasticity for the compression of the surface. From Figure 7 it may be seen that the magnitude of E is of great importance for the resulting pressure. We can first regard the modulus for a fabric with a smooth surface. An experimental determination of the modulus is difficult, because we have to deal with the force necessary to bring the yarns of the fabric closer and not with the elastic properties of the fabric in the usual sense. This force can be assumed to be of the same order of magnitude as the force necessary to straighten the yarns of the fabric, which can be determined experimentally.

The stress-strain curve was determined for a cotton fabric, and the modulus of elasticity was determined for the first part of the curve, which corresponds to a straightening of the yarns. The lowest value obtained was 10,000 g. per sq. cm. The value for E of this order of magnitude will lower the effective pressure by a very small amount, which is of no practical importance.

If the fabric surface is covered with a fiber felt—*e.g.*, a raised woolen fabric—E is of the same order of magnitude as the compressibility of fiber pellets—*i.e.*, between 1 and 100 g. per sq. cm. Figure 7 and the theoretical aspects show that the effective pressure will be much less in this case.

The experiment performed by Baxter and Cassie can be understood also from these relationships. The gabardine, on account of the higher modulus of elasticity of its surface layers, was affected by a much higher pressure than was the wool gauze with the porous fiber felt on the surface. The velocity of the waterdrops is unknown, but if we suppose two fabrics of the construction described above to be affected by raindrops with a velocity of about 500 cm. per sec., the gabardine should be affected by a mean pressure of about 80 g. per sq. cm., according to equation (13), whereas the wool gauze should be influenced by pressures below 10 g. per sq. cm., assuming E to lie between 2 and 20 g. per sq. cm. This value was obtained from Figure 7. The theory developed shows that the lower portions of the dotted- and the solid-line curves give the upper limit of the pressure.

Structure of Water-Repellent Fabrics

Some conclusions of practical value for the construction of water-repellent fabrics can be drawn from the pressure relationships during the impact.

Fabrics with plain surfaces—*e.g.*, cotton fabrics of the type often used in raincoats—will be affected by high pressures during short periods. Such fabrics must therefore be constructed to withstand

* In the above examples the values of p_0 were taken from average values of the hydrostatic pressure test and from the article by Baxter and Cassie [1]. We are very indebted to Dr. Earl K. Fischer and Dr. Helmut Wakeham for calling to our attention the fact that p_0 could be calculated from the following expression:

$$pr = -2\sigma \cos\theta,$$

where p is the pressure required to force water into a pore of radius r, σ is the surface tension of water, and θ is the contact angle between water and the pore wall. If water does not wet the fabric, θ will be larger than 90° and $\cos\theta$ will be negative. There will then be a positive pressure required to force water into the fabric, which is inversely proportional to the pore radius. Actually, if $\sigma = 72$ dynes per cm. and $\theta = 180°$ for a water-repellent surface, r will have a value of about 15 microns (0.015 mm.) when the pressure is 50 g. per sq. cm. This value agrees well with those observed, which indicates that the value of p_0 assumed is of the right order of magnitude. Since the submittance of this manuscript, a study of pore-size distribution has been published by Burleigh, Wakeham, Honold, and Skau (TEXTILE RESEARCH JOURNAL **19**, 547 (1949)).

these pressures. They should be tightly woven and should have no holes due to faulty weaving. A fabric with a highly compressible surface will be affected by a much lower pressure, and small irregularities in the weave construction will be of less importance. A napped fabric, preferably with the nap in a longitudinal direction, should meet these requirements. Woolen fabrics of this type have been used for coats in Sweden known as "Loden" coats. With a good water-repellent finish, these coats are reported to be effective as rain-resistant garments.

If the apparent contact angle between the water and the fabric is less than 90°, water will be absorbed by the capillaries. In this case the highly porous surface will be of little value and will absorb large amounts of water. The aspects of the fabric structure given above are founded only on the pressure relationships existing during the impact of a raindrop and do not involve the conditions for wettability of the fibers. It is interesting, however, to note that a porous fabric surface also meets the requirements for low wettability—*i.e.*, high apparent contact angles and unstable water films between the fibers.

Testing of Water-Repellent Fabrics

Some conclusions regarding the testing of water-repellent fabrics can be drawn from a study of the pressure exerted by raindrops.

It is a well-known fact that the type of support has a great effect on the amount of water penetrating through the fabric. If a rigid support is used, a larger amount of water will pass through as compared with a more elastic support. The effect of different types of supports in a rain tester has been investigated [4]. Much more water passed through the fabric when the backing was made from a wire net with small meshes (0.3-mm. side) as compared with a wire net with larger meshes (10-mm. side). With the latter net, the penetration first occurred at the places in contact with the wires. It is also well known that leakages of rain usually occur first at the shoulders, where the coat is supported.

These examples demonstrate the effect of the pressure on the penetration of a fabric by water. If the backing is rigid, the fabric cannot yield to the drop, and the pressure will be described only by equation (16). Figure 7 shows that high pressures result when $E \geq 2 \times 10^4$ g. per sq. cm., which is usually the case with plain fabrics.

There are several methods for testing water-repellency. Using the du Pont rain-tester, a high correlation with rain-room data was obtained for cotton fabrics [6]. The fabrics investigated had to withstand rather high pressures in the testing apparatus if they were to keep the rain out for a longer time in the rain room.

This confirms our theory that plain fabrics must be constructed to withstand high pressures. Test methods of this kind, which can be very useful for the comparison of fabrics of the type used in the paper cited, will probably not be suitable for the testing of fabrics with compressible surfaces. These fabrics will be expected to show poorer performance in the rain tester than in a natural rain, since the water jets will very soon compress the surface layers. The jets, it is true, are split into droplets before they strike the fabric, but the drop intensity is very high. The fabric will therefore not have time to recover from the impacts, but will be subjected to a continuous pressure.

If we wish to get information on the performance of a fabric in rain, testing in artificial rain seems to be the most suitable method, since the very complicated physical course during the impact could hardly be simulated in any other way. For reasons given above, the drop intensity should not be too high. Furthermore, the velocity of the drops will have considerable effect on the result, as will also the elasticity of the backing material.*

Summary

When a drop of water strikes a solid foundation a pressure arises between the drop and the foundation. This pressure is a function of time. From studies of the course of impact with high-speed motion pictures, the change in the shape of the drop during the impact was determined. A hydrophobic cotton fabric and a thin acetate film were used as foundations in the experiment. The photographs showed that the upper part of the drop retained its spherical shape and had the same velocity as at the beginning of the impact, while the water in the lower part of the drop was pressed outwards as a continuous film. The center of gravity of the deformed drop could thus be experimentally determined, and the calculation of the pressure was

* A new type of rain tester, proposed as Swedish standard apparatus, has been investigated at the Swedish Institute for Textile Research and compared with other test methods. The results of this investigation will be published.

founded on the law of motion of the center of gravity.

The result of the calculation is that the pressure can be limited upwards by two equations, one of which is dependent upon Young's modulus of elasticity of the surface layer of the foundation. When this modulus is low—*e.g.*, 2 g. per sq. cm.—there is a low pressure during the whole course of impact. A foundation with a high modulus will be affected by a rather high pressure during a short time. In this case the pressure has assumed a low value when the deformation of the drop is about half of its radius. The time necessary for such a deformation is dependent upon several factors. For the actual conditions during the experiment, it is about 5×10^{-4} sec.

The depth of penetration of the first drop into a fabric with plain surface was found to lie between 0.1 and 0.3 mm. if the pressure required to force water through the fabric was between 50 and 25 g. per sq. cm. The magnitude of the modulus of elasticity of the surface layer was found to be higher than 10^4 g. per sq. cm. for a plain cotton weave, but between 1 and 100 g. per sq. cm. for a napped surface. The plain fabric will therefore be affected by much higher pressures in rain than the napped one. If a fabric with a plain surface is to be effectively rain-resistant, it must be constructed to withstand these pressures. Small irregularities in the structure of a napped fabric will be of less importance.

Use of artificial rain is the most suitable as a test method for water-repellency, since the complicated physical course during the impact could hardly be simulated in any other way.

The elasticity of the backing material and the velocity of the drops greatly influence the amount of water penetrating the fabric. The drop intensity should not be too great; otherwise the fabric surface will not have time to recover from the impact. This is especially important for highly compressible surfaces such as napped fabrics.

Acknowledgment

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Microbiological Degradation of Cellulose*

Glenn A. Greathouse†

Introduction

The effects of microbiological degradation of materials have only within the past decade been subjected to a systematic inquiry. The seriousness of the problem, however, has been recognized for many years. Even though the importance of the damage and losses of cellulosic materials during World War II has been emphasized many times, in the United States the damage caused by microbiological attack on fabrics, rope, wood, and other cellulosic materials is still reliably estimated to be several million dollars annually.

Considerable knowledge of the number and the destructiveness of microorganisms which degrade cellulose, their control by chemicals, and the resistance of chemically modified cellulose to these agents has been obtained through this systematic inquiry. But no panacea against ultimate deterioration has been discovered. The more recent knowledge has been applied by manufacturers of textiles and finishes, and as a consequence the service life of these materials has been lengthened.

The exact mechanism of microbiological attack on cellulose is not known, but various theories have been advanced. An attempt will be made to clarify some of our reasoning about this mechanism by reviewing recent studies, by presenting additional unpublished data obtained during 1940–43 while the author was an emmployee of the U. S. Department of Agriculture, and by comparing these findings with data which have been published or which are available to the author.

Causal Microbiological Agents

Cellulose-decomposing activity of fungi is widely distributed but not universal among all genera or species. This knowledge has been obtained through the efforts of many investigators in many laboratories. The earliest paper of importance presenting experimental evidence on cellulose decomposition by fungi appears to be a report by van Iterson in 1904 [21]. In the years between 1913 and the present, the U. S. Department of Agriculture has investigated and reported on the ability of many microorganisms to decompose cellulose [27, 28, 30]. The Philadelphia Laboratory of the Office of The Quartermaster General has been active in this field since its establishment in 1944 [53–56, 61, 62, 64]. Other laboratories in the United States and abroad have likewise pursued these studies.

Marsh and coworkers [30] recently pointed out that much of the information obtained before 1934 on the degradation of cellulose by fungi involved the use of unsatisfactory experimental methods, with the consequence that many of the results obtained were inconclusive. These authors have given an excellent critical review of the available literature and additional data on 420 fungus isolates.

Before 1942 most, if not all, procedures for evaluating the cellulolytic degradation properties of fungi utilized carbon sources other than cellulose. In 1942 Greathouse and his associates described a new glass-wick, culture-bottle technique for testing the cellulolytic activity of fungi, in which the sole source of carbon for the fungus was cellulose [16]. This technique has been extensively used and has aided in clarifying the cellulolytic properties previously reported for a particular fungus.

A review of the investigations of many workers reveals that cellulolytic activity of fungi occurs with a high degree of regularity among one or more isolates of the following 35 genera: *Acremonium, Alternaria, Aspergillus, Brachysporium, Cephalosporium, Chaetomium, Cladosporium, Coccosporium, Corticium, Curvularia, Diplodia, Fusarium, Gliocladium, Gliomastix, Glomerella, Helminthosporium, Hendersonia, Humicola, Memnoniella, Monotaspora, Myrothecium, Neurospora, Penicillium, Phialophora, Phoma, Sclerotinia, Scopulariopsis, Sordaria, Stachybotrys, Stemphylium, Stysanus, Thielavia, Torula, Trichoderma,* and *Verticillium*.

Of particular interest is the recent investigation by White and coworkers [64] on the cellulolytic activity among the isolates of the genus *Aspergillus,*

* This paper was presented at the 116th Meeting of the American Chemical Society, Atlantic City, September, 1949.

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since this group has been considered by some to be of little importance in the degradation of cellulose, being only a superfluous growth on the finishings of textiles. They concluded from their experiments that cellulolytic activity is absent in the *A. niger* and the *A. carbonarius* subclasses of this genus, but that it is a fairly constant characteristic of the *A. luchuensis* subclass. This is in agreement with the experiments of Klemme and associates on *A. niger* [28]. Marsh and coworkers [30] have presented proof for cellulolytic activity in 10 of the 14 groups instead of in 5 as shown by White and associates [64]. Of equal importance is the study of 140 isolates of the genus *Penicillium* by Marsh and coworkers [30]. They found cellulolytic activity rather widely distributed among species of the genus *Penicillium;* however, certain series showed no activity—*viz., P. frequentans, P. lividum, P. adametzi,* and series of other species. Apparently, *Mucor, Rhizopus,* and other genera of the Mucoraceae do not contain any active cellulolytic species [30]. The literature rarely mentions the cellulolytic properties of actinomycetes.

Although many organisms have been shown to be potentially capable of deteriorating cellulose, some of them are more common and more important than others. Thom, Humfeld, and Holman [50] were the first to point out the value of *Chaetomium globosum* for use in evaluating preservatives applied to awnings and similar fabrics. Since that time, this organism has been designated as the test fungus for many specifications for various fabrics. Many other reports give additional information on *C. globosum* and other *Chaetomium* species [16, 17, 28, 31, 40, 50, 61].

Memnoniella echinata has been mentioned repeatedly as being of very common occurrence on textiles in tropical exposures [51, 61]. This fungus is a close relative of *Stachybotrys,* which is frequently observed on mildewed cotton fabrics. However, Marsh and associates found representatives of the genera *Alternaria, Fusarium,* and *Cladosporium* to be the more prevalent fungi on field cottons [29].

One of the most active cellulolytic fungi isolated to date is *Myrothecium verrucaria,* USDA 1334.2, which was isolated and shown to have high cellulolytic activity by Greathouse in 1940. Later it was tentatively identified by Charles Thom as *Metarrhizium* sp. [16], and subsequently described by Pope [38] as *Metarrhizium glutinosum.* Still later it was shown by White and Downing to be a misnamed isolate of *Myrothecium verrucaria* [63]. Many investigators have now confirmed its strong cellulolytic activity. The Philadelphia Laboratory of the Office of The Quartermaster General has published several reports since 1944 on the cellulose degrading properties of this organism, as has the U. S. Department of Agriculture [16, 28, 31, 38, 41, 55, 63].

More has been accomplished in the isolation, identification, and determination of cellulolytic activity of fungi than of bacteria. Waksman stated that fungi play a more active role than bacteria in the decomposition of cellulose in the soil [58]. Levinson and Di Lello [53] recently studied several soil bacteria and conclude that there is insufficient data to assume that bacteria play only a minor part in the soil decomposition of cellulose.

A review of the literature reveals that aerobic bacteria of the genera *Cytophaga, Cellulomonas,* and *Vibrio* are the most important in cellulose decomposition; but anaerobic bacteria show this activity in waterlogged soils, in peat bogs, and in cellulose digestion in animal stomachs [20, 58].

Spore-forming bacilli have rarely been found to be active in the decomposition of cellulose; *Bacillus polymyxa* and *B. macerans* have been reported to possess feeble cellulose-decomposing power, but they are not ordinarily regarded as being cellulolytic. Kalnins described *B. latvianus* [22], Fuller and Norman reported on *B. aporrhoeus* [12], and Kellermann and McBeth referred to *B. amylolyticus* as having cellulolytic properties [27].

During World War II some 1,100 strains of bacteria were isolated by Reuszer from deteriorated fabrics [52]. Approximately 150 of these proved to be cellulolytic. Levinson and Di Lello evaluated 41 strains of cellulolytic bacteria by determining their ability to lower the breaking strength of cotton sheeting [53]. Of these there were 5 members of the *Cytophaga* group, 12 unipolar flagellated organisms of the genus *Vibrio,* 6 *Corynebacteria,* 3 species of *Cellulomonas,* and 4 *Actinomycetes.* Of 26 strains of micrococci tested none were capable of decomposing cellulose. Further information can be found in reports by Fahraeus [9] and Stanier [45].

Mechanism of Degradation of Cellulose

1. Effect of Fungal and Bacterial Attack on Cotton Fibers

The penetration or attack of cotton fibers by fungi requires further investigation. There is a diversity

of opinion as to whether or not fungi penetrate the lumen and degrade the fiber from the inside out. Weston [60] presented a photomicrograph showing penetration of the fiber wall by fungus filament and two drawings to illustrate (1) the penetration of the fiber wall by *Myrothecium verrucaria* (*Metarrhizium glutinosum*) and its initial growth in the central canal, and (2) *Memnoniella echinata* hyphae in the lumen of a fiber. Zuck and Diehl [65] published a photomicrograph showing a portion of a fiber of cotton duck within which was located a dematium-like hypha after the cloth had been exposed 18 mo. in Florida. Marsh and coworkers [30] presented photomicrographs of *Cladosporium herbarum* illustrating the position of hyphae on the outside of the fiber only; they are of the opinion that some fungi seem not to enter the lumen.

The manner in which bacteria have been observed to attack cotton fiber is somewhat different from that of fungi. The bacteria adhere to the outer surface of the fiber and corrode inwardly. Hence, fibers badly degraded by bacteria will appear roughened and pitted on the surface, the inner wall usually remaining even in outline and morphologically unaffected. Stanier [45] presents photomicrographs illustrating the action of bacteria on cotton fibers.

Basically, both fungi and bacteria degrade cellulose by the action of their enzyme systems. Attack is accompanied by great losses in tensile strength and small losses in weight. Results obtained by the author for cotton fibers inoculated and incubated with *Myrothecium verrucaria* are presented in Figure 1. By soaking the fibers in sodium hydroxide, however, it was found that the site of attack is soluble in the alkali; the concentration of alkali needed in order to observe the extent of attack decreases with increasing incubation time. Microscopic observations yielded the following information: fibers incubated for 12 hrs. and exposed to 11% sodium hydroxide solutions at room temperature showed small, random, corroded notches, whereas similarly incubated fibers exposed to 7% alkali had no corroded areas which were microscopically visible. On the other hand, if fibers which had been incubated for 24 to 48 hrs. were exposed to 7% solution, the corroded areas were plainly visible. In fact, the 48-hr. fibers showed corroded areas even after they were washed in distilled water. These observations indicate that *Myrothecium verrucaria* vigorously attacks the fiber from the outside. Using this technique, no attack was

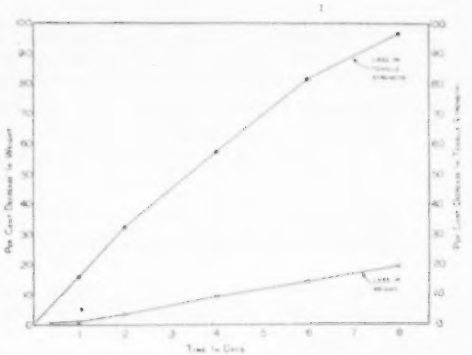

FIG. 1. *Loss in weight and tensile strength of Stoneville 2B cotton fibers which had been inoculated and incubated with* Myrothecium verrucaria. *Results are the averages for 10 replicates.*

observed in the lumen. The attacked fibers did not give the usual bead effect on swelling in cuprammonium. These observations of fiber corrosion and lack of bead effect on swelling in cuprammonium confirm the findings of earlier investigators. This appearance of notches indicates the change in solubility or dispersibility of the areas when the fungus enzymes have been active and may aid in understanding the data for great loss in tensile strength accompanied by small weight losses. Further studies of this nature have been conducted by the Institute of Textile Technology, Charlottesville, Virginia.

The above observations on the alkali solubility of biologically attacked cellulose are of interest in the light of Mark's work [32]. Mark stated, on the basis of the relationship which exists between degree of polymerization and alkali solubility of cellulose, that it should be possible to separate the shorter-from the longer-chain material by extraction with alkali. In fact, such a separation is accomplished when the α-cellulose fraction is isolated from the cellulosic material and the β- and γ-cellulose fractions are left in solution. Moreover, by employing alkali solutions of varying concentrations, or of constant concentration but of decreasing temperatures, it is possible to subdivide the long-chain α-cellulose still further. This information is pertinent to the preparation of biologically degraded cellulose for fluidity measurements (to be mentioned later).

In Table I are presented some chemical characteristics of cotton fibers which had been inoculated and incubated with *M. verrucaria*, as found by the

TABLE I. CHEMICAL CHARACTERISTICS OF BUNDLES OF FIBERS, STONEVILLE 2B, AFTER EXPOSURE TO *Myrothecium verrucaria* *

Days after inoculation	Alkali solubility	Copper number	Fluidity (rhes)	Loss in tensile strength (% of original)
3	4.89	0.46	4.36	40.5
7	6.98	0.98	5.02	94.1
14	7.42	1.01	6.55	100.0
Control	3.58	0.32	4.15	—

* Ten replicates were used in each experiment.

author. The methods of determining alkali solubility, copper number, and fluidity are given in the Appendix, section A.

Data on the alkali solubility and copper numbers are in general agreement with those of other investigators. Alkali solubility is a rough measurement of the degree of polymerization; the copper number of cellulose varies directly with the amount of degraded cellulose of an aldehydic or ketonic structure. These values, therefore, are measures of the chemical deterioration of cellulose.

The fluidity data indicate greater changes with microbiological degradation than those reported by some investigators. Changes in fluidity accompanying extensive microbiological attack on cotton fabric were reported by Searle [42] and by Heyes and Holden [19] to be insignificant or absent, and by Rogers, Wheeler, and Humfeld [40] to be very slight, not exceeding 10% of the original value after extreme tendering by *C. globosum* or *Spirochaeta cytophaga*. Rutherford [54] showed that severe tensile strength losses of cotton under the influence of *C. globosum* are not accompanied by measurable changes in cuprammonium fluidity, but he found that exposure to the sun resulted in very large fluidity increases. Dean and Worner [7], using fabric highly tendered by *M. verrucaria* (*Metarrhizium glutinosum*), found cuprammonium fluidity to be essentially unchanged by microbiological action.

Unpublished cuprammonium fluidity data supplied by Dr. Carl M. Conrad (Table II) on cotton fibers which had been inoculated with *C. globosum* and incubated for 28 days are of interest with respect to the data presented in Table I and the findings of the above-mentioned investigators. These data of Dr. Conrad show a marked increase in fluidity with microbiological attack, even more marked than the author's data (presented in Table I).

One might inquire about the reason for these contradictory results for the fluidity of cellulose degraded by microorganisms. In the author's opinion some of the discrepancies might be traced to the method of preparing the sample for fluidity determination. It has been shown that the solubility or dispersibility of biologically degraded cellulose in alkali or water increases with incubation time. Consequently, if the cellulose sample is washed in running water or is otherwise treated to remove the mycelium or by-products of the fungus, a large percentage of the more soluble or dispersible chain molecules would be lost. Therefore, if most of the more soluble or dispersible molecules are removed

TABLE II. CHEMICAL CHARACTERISTICS OF BUNDLES AND MATS OF COTTON AFTER DETERIORATION BY *Chaetomium globosum* FOR 28 DAYS *

Sample No.	Preparations	Moisture (%)	Alkali solubility (%)	Copper number	Fluidity (rhes)
1230CX	Bundle	3.72	6.98	1.01	8.83
1231CX	Bundle	3.68	5.55	0.95	7.38
Average	Bundle	3.70	6.26	0.98	8.11
1232CX	Mats	3.56	5.74	0.96	10.35
1233CX	Mats	3.68	5.92	0.78	9.05
Average	Mats	3.62	5.83	0.87	9.70
Regional var. average		3.09	3.78	0.32	3.56
No. of samples		18	112	112	112

* By permission of Dr. Carl M. Conrad.

by the preparation of the cellulose sample for fluidity measurements, the longer, unmodified molecules should give the same fluidity as that of the original cellulose sample. The author realized that the degree of accuracy of fluidity measurements on microbiologically degraded cellulose is less than on cellulose containing no fragments of mycelium or other substances resulting from fungus attack. It should not be forgotten that the ratio of the undamaged to the damaged portion of fibers may be large under certain experimental conditions, and even when these precautions are taken little difference in fluidity should result.

The mechanism of the action producing great losses in tensile strength with relatively small changes in the chemical characteristics of cellulose is still not known. Fractionation of microbiologically degraded cellulose by means of the ultracentrifuge might be useful, along with other chemical analyses, to explain the results obtained for fluidity and decrease in tensile strength of cotton fibers.

The decrease in strength resulting from exposure of cotton yarn to cellulose-destroying bacteria was investigated by Staudinger and his coworkers [46]. By determining the degree of polymerization of the cellulose of untreated and treated samples of a used fishing net and of nitrated products obtained from these, it was found that the decrease in strength was not the result of any appreciable decrease in degree of polymerization. Walseth [59] obtained similar results with weight changes by using enzyme preparations.

In the work by Staudinger and associates it was suggested that the decomposition of cellulose by bacteria proceeds from the end groups of the molecule, whereas attack on cellulose by fungi results in a splitting of the molecule in the middle. Clayson [5] concluded from a review of the available literature that the cellulolytic action on the molecule proceeds end-wise. This was based particularly on the work of Grassmann *et al.* [15]. Siu and associates [44] concluded from their results in weight loss on low acetyl-content cotton samples which had been inoculated with *Myrothecium verrucaria* that the organism can attack a glycosidic linkage or an unsubstituted anhydroglucose unit at any position in the cellulose linear chain. Walseth's data [59] and data presented later by the author indicate that cellulolytic enzymes attack in a random fashion.

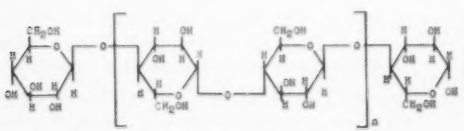

Fig. 2. *Molecular chain formula for cellulose.*

2. Relationship Between Molecular Structure and Microbiological Resistance, as Determined with Cellulose Derivatives

The general plan used by the author in 1940 to study the problem of molecular structure and microbiological resistance was: (1) to determine the functional group or groups in the cellulose molecule which must be blocked in order to prevent microbiological utilization; (2) to evaluate cellulose and sugar derivatives which have been blocked in the essential group by substituents which impart other desirable qualities to cellulose; and (3) to use this information in developing practical methods of protecting cotton fabrics from rot and mildew.

The structural chain formula of cellulose, as it is generally accepted today, is shown in Figure 2.

The reactivity of the molecule is mainly due to the presence of the primary ($-CH_2OH$) and secondary ($=CHOH$) alcoholic groups. The nature and extent of chemical modification is quite variable, ranging from simple oxidation of these groups, as in oxidized cellulose, to substitution with more complex groups. The maximum possible substitution, as indicated in Figure 2, is three groups per anhydroglucose unit.

It is necessary to obtain a better knowledge of the process of chemical conversion undergone by the cellulose molecule during microbiological degradation in order to devise methods of preventing the mildewing and rotting of cellulosic materials. Considerable work has been started with this goal in mind [16, 24, 25, 26e, 35, 39, 40, 41, 44, 46, 55, 56, 59].

In 1940, when the author undertook the project on deterioration of cotton for the U. S. Department of Agriculture, limited information was available on the resistance of cellulose derivatives, in the absence of other carbon sources, to pure cultures of cellulolytic microorganisms. It has long been known that cellulose can be made resistant to microbiological attack by altering the molecule. In 1921, Dorée reported that the monoacetate derivatives of cotton were resistant to the microbiological action of sea

water [8]. During the period from 1925 to 1939, Karrer and coworkers [23–26a–f] and Thaysen and his associates [47, 48] reported that cellulose acetate was resistant to microbiological attack. These observations have since been confirmed by several investigators, including Heyes and Holden [19], Borlaug [3], Goldthwait [14], and Siu *et al.* [44].

In order to obtain additional information on these findings, cellulose derivatives substituted at known positions in the molecule by selected substituents were evaluated for resistance to attack by *M. verrucaria*. The cellulose derivatives were the sole source of carbon for the fungus in these preliminary experiments, but necessary mineral salts were supplied. The following cellulose derivatives were found to be completely or highly resistant to attack by this organism: 3 cellulose acetates, obtained from the Hercules Powder Company, containing 9.3%, 22.4%, and 30.0% acetyl, determined by the Eberstadt method of analysis [13]; cellulose triacetate (Appendix, section B); ethylcellulose, obtained from the Dow Chemical Company, 45.8% ethoxy by analysis; methylcellulose, obtained from the Dow Chemical Company, degree of substitution 2.0; and 6-cyanoethylcellulose, containing 1.7 CN groups per anhydroglucose unit.

Cellulose acetate with 3.4% and 5.1% acetyl, cellulose-6-nitrate, and 6-carboxycellulose supported some growth of the fungus. Burkholder and Siu reported that acetylated cellulose of 3.24%, 4.78%, 5.21%, and 9.71% acetyl lost 52.8%, 49.3%, 48.4%, and 19.8% by weight, respectively, after 10 days of incubation with *Sporocytophaga myxococcoides* [56]. These data suggest that the resistance of the cellulose molecule to attack by *M. verrucaria* can be attributed to a chemical blocking of the hydroxyl groups. Having obtained the information on the resistance of cellulose derivatives to *M. verrucaria*, derivatives of glucose and cellobiose were prepared and evaluated using the same cellulolytic fungus. These studies showed that the availability of these sugars is decreased by chemical substitution in the hydroxyl groups. Cellobiose octacetate and pentacetyl glucose were completely resistant to the attack of *M. verrucaria*, as was cellulose triacetate. These data confirm the behavior of the fungus on homologous cellulose derivatives. Siu and associates in 1949 [44] investigated the susceptibility of 9 glucose, 3 mannose, and 3 cellobiose derivatives to 9 different fungi; and of 11 cellulose derivatives to *M. verrucaria*. They concluded: "As long as there was at least one firmly bound substituent in every anhydroglucose unit, the resulting derivative was not susceptible to microbiological attack." Their results, in general, agree with the author's preliminary findings when a similar derivative was evaluated. Freeman and associates [10] found that in the presence of mineral nutrients and a rich bacterial flora at 25°C, solutions of sodium carboxymethylcellulose are subject to a rapid loss of viscosity unless suitable bacteriostats are added.

3. Cellulase Enzymes

Information on cellulolytic enzyme activity dates from 1886, when de Bary found that he could dissolve cell-wall constituents of plants by the application of an extract from the mycelium of the fungus *Peziza sclerotiorium* [2]. The enzyme was called cytase. He did not differentiate the cell-wall components and did not identify the products formed. Since this time, cellulolytic enzyme preparations which are active against various forms of cellulose have been reported by several investigators. Among the organisms employed for preparing such extracts were:

Aspergillus oryzae—Grassmann and associates [15]
Aspergillus oryzae—Freidenberg and Ploetz [11]
Bacterium bosporum—Kalnins [22]
Bacterium protozoides—Kalnins [22]
Cellulobacillus myxogenes—Simola [43]
Cellulobacillus mucosus—Simola [43]
Coniophora cerebella—Nord and Vitucci [35]
Cytophaga globulosa—Fåhraeus [9]
Merulius lachrymans—Ploetz [36]
Myrothecium verrucaria—Greathouse [18] (and data reported herein)
Myrothecium verrucaria—Saunders and associates [41]
Plectridium cellulolyticum—Pochon [37]
Sporotrichum carnis—Vartiovaara [57]
Various thermophilic bacteria—Pringsheim [39]

Active cellulolytic extracts have also been prepared from the intestinal juices of the snail *Helix pomatia* [26e] and from the protozoan *Eudiplodinium neglectum*, which is isolated from cattle rumen [20]. The general nature of enzyme-substrate contact and the hypothesis of intermediate compound formation which has been generally postulated for enzyme actions have been reviewed elsewhere [4, 9, 33, 34, 49].

According to the view now commonly accepted, an enzymic hydrolysis of the long-chain polysaccharide must be the first step by which fungi and bacteria consume cellulose. The ultimate stages of decomposition occur only after extracellular hydrolytic enzymes secreted by the organism have converted the cellulose into simple sugars or soluble products which are capable of being absorbed by the cell of the microorganism; intracellular enzymes may then complete the decomposition to the metabolic products normally observed—*e.g.*, gases and acids.

A characteristic of enzymes which might affect the nature of the enzymic hydrolysis of cellulose is the marked specificity which they generally exhibit. A major problem is to learn whether or not the enzyme or enzymes specifically catalyze the removal of glucose units at the ends of a cellulose chain or at random along the chain. If enzymes attack in an endwise fashion, the initial degree of polymerization can be expected to have a marked effect on the rate of hydrolysis, since the number of end groups would increase with a decrease in degree of polymerization. If the attack were random, on the other hand, the degree of polymerization should have little effect on hydrolysis. In an attempt to reach some conclusions on this mechanism of action, a polyhomologous series of hydrocelluloses was prepared (Table III). The method of preparation is given in the Appendix, section C. Data presented in Table III and data of Walseth [59] indicate the latter type of attack. Walseth states that no significant relationship between the ease of enzymic hydrolysis of cellulose and the degree of polymerization is apparent from the results of his studies. Both the author and Walseth used cotton having a low degree of polymerization compared with that of native cellulose of unmodified cotton fibers. The results shown are in agreement with those recently reported by Siu and associates [44], but are at variance with Clayson's end-wise attack theory [5].

Many previous investigators have made special attempts to prepare the cellulose samples having the smallest possible particle size in order to increase the rate of dissolution by enzymic action. Although the size of particle influences the rate of hydrolysis, this is also true of the internal surface which is accessible to the enzymes. Consequently, the amount of crystalline and amorphous forms available should be a factor in the rate of dissolution by enzymic action. Walseth [59] prepared cottons which would be reactive to different degrees by swelling them in phosphoric acids, and found an increase in the rate of hydrolysis with increased swelling or dispersion. In the resulting hydrated cellulose, the hydroxyl groups of the extended crystal lattice were more accessible, and the cellulose had a higher water sorption capacity. By using a cotton which had been treated with phosphoric acid so that it had a degree of polymerization of 1215, he found a loss in weight of 10% within 1 hr. of reaction with a commercial enzyme preparation; 25.6% in 5 hrs.; 70.5% in 82 hrs.; and 79.3% in 144 hrs.

Since cellulose enzymes vary to some extent with the source, it is difficult to list their properties, especially in so far as the optimum pH of activity is concerned. The reports of various workers concerning the optimum pH for cellulase from several sources are listed in Table IV.

The effect of varying pH values on the extent of

TABLE III. Properties of Hydrocelluloses of Varying Degrees of Polymerization

D.P.*	Reaction time	Residual free acidity† (pH)	Degradation by *M. verrucaria*‡ (% of original dry wt.)
1675	0	—	42.4
830	10 min.	6.30	47.8
400	30 min.	6.37	40.6
120	25 hrs.	6.25	48.2

* Average of cuprammonium and nitrate values.

† Determined by suspending 1.0 g. hydrocellulose in 50 ml. boiled, distilled water, allowing to stand 24 hrs., and making pH measurements with a glass-electrode Beckman pH meter.

‡ After 4 days incubation; values not corrected for presence of dried mycelium in residue.

TABLE IV. Optimum pH of Activity for Cellulases, as Reported by Various Investigators

Investigator	Source of cellulase	Optimum pH
Karrer, 1923	*Helix pomatia*	5.28
Ziese, 1931	*Helix pomatia*	4.0 to 4.5*
Ziese, 1931	Barley malt	3.0*
Grassmann, 1933	*Aspergillus oryzae*	4.5
Freidenberg and Ploetz, 1939	*Aspergillus oryzae*	4.5
Freidenberg and Ploetz, 1939	*Helix pomatia*	5.2 to 5.4
Greathouse, 1940-43	*Myrothecium verrucaria*	5.0
Fåhraeus, 1947	*Cytophaga globulosa*	7.0†
Saunders and associates, 1948	*Myrothecium verrucaria*	5.5
Walseth, 1948	Rohm & Haas enzyme preparation	4.5

* Substrate was hydroxyethyl-cellulose rather than cellulose.

† Substrate was lichenin rather than cellulose.

TABLE V. OPTIMUM TEMPERATURE OF ACTIVITY FOR CELLULOLYTIC PREPARATIONS OF *Myrothecium verrucaria*; SUBSTRATE, BALL-MILLED COTTON

Incubating temperature (°C)	Cellulose hydrolyzed (%)
20	10.1
30	10.8
35	14.2
40	17.1
45	10.9
50	3.8

hydrolysis by an enzyme preparation obtained from *M. verrucaria* is shown in Figure 3.

The optimum temperature of activity for the isolated cellulases reported also varies. Pringsheim [39] stated that optimum activity occurred at 46°C, but that cellulase was active over a range of from 20°C to 70°C. Karrer [24, 25] reported that inactivation of cellulase from the snail begins at 45°C to 50°C, is considerable at 55°C, and is almost complete at 60°C. Fåhraeus [9] found the optimum temperature to be 36°C; the author, 40°C (see Table V); and Saunders and associates [41], 40°C, with rapid inactivation above 50°C.

Although the data presented by the various investigators are certainly suggestive of true cellulolytic enzyme activity, nevertheless the earlier workers, in general, have not conclusively established the cell-free nature of their preparations. Questions have been raised about the possibility of bacterial or fungal contamination during evaluation of this activity, which frequently requires several days. These doubts, plus the discovery of the very rapid cellulolytic activity of the fungus *M. verrucaria* (*Metarrhizium glutinosum*), USDA 1334.2, in 1940, were responsible for the initiation of the cellulase study herein reported. Information concerning the rapid cellulolytic activity of this organism was widely disseminated during World War II for use in problems relating to cellulose decomposition. Accordingly, Saunders, Siu, and Genest [41] used *M. verrucaria* (isolate number 1334.2) in their studies.

Preparation of Extracts from *Myrothecium verrucaria* Containing Active Cellulases

The results reported here on the cellulolytic activity of *M. verrucaria* are considered only preliminary. Much remains to be done on these enzyme systems.

The method used in the preparation of these cellu-

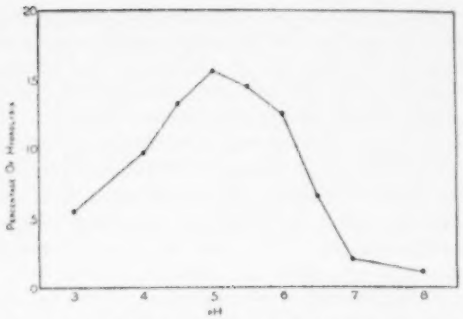

FIG. 3. *Optimum pH of cellulolytic enzyme preparations. (5 ml. of crude enzyme preparation obtained from* Myrothecium verrucaria *and 1% cellulose.)*

lase extracts is given in the Appendix, section D. Extracts prepared from *M. verrucaria* naturally contain several enzymes, some of which are not directly engaged in the decomposition of cellulose. But the enzymes considered here are those associated with the hydrolysis of cellulose to glucose or those which produce losses in the tensile strength of cotton fibers.

Extracts of young cultures of *M. verrucaria* yielded more consistent and active enzymes than did the older, especially when dewaxed cotton fibers were utilized as the substrate. It is the author's opinion that the enzyme or enzyme complex capable of first attacking natural cotton cellulose, whether it be breaking the cross-linkages or attacking the cellulose molecule, is produced by the young fungus mycelium near the tip of the hypha and diffuses only a short distance. This is borne out by microscopic observations and by the fact that more consistent and active preparations are obtained from 5- to 7-day-old cultures than from 10-day-old or older cultures when the substrate is natural cotton. Most previous investigators have found little or no activity on substrates other than such materials as cellophane, filter paper, and lichenin.

Attempts were made to determine whether *M. verrucaria* produced extracellular enzymes which are capable of hydrolyzing cellulose. Extracellular enzymes were found in the filtrates, but additional activity was obtained with a technique in which both the filtrate and the extract of mycelium pellets were used (Appendix, section D).

An index of the cellulolytic activity of *M. verrucaria* extracts was obtained for different types of

TABLE VI. Effect of Cell-Free Cellulolytic Preparations of *Myrothecium verrucaria* on Cotton Cellulose After 48 Hours

Substrate	Cellulose (as glucose) (%)	Loss in wt. (%)	Loss in tensile strength (%)
Ball-milled cotton	16.8	20.2 ± 4	—
Dewaxed cotton fiber	9.4	7.5 ± 2	32.6 ± 3
Ball-milled cellophane	27.0	—	—

cotton cellulose, as presented in Table VI. The technique used in obtaining these results is described in the Appendix, sections E and F.

Results for 24- and 96-hr. incubation periods yielded in general the same data, except that the 96-hr. results were slightly higher, particularly when the entire fibers were used as substrate.

The results of Figure 4 tend to confirm the statement of Karrer [26d] that in order to obtain maximum hydrolysis of cellulose, solutions of the highest possible concentrations are required—*i.e.*, the highest ratio of enzyme concentrations to cellulose.

The major product of enzymatic hydrolysis of cellulose was found to be glucose (Appendix, section F).

Summary and Conclusions

Cellulose-decomposing activity of fungi is widely distributed, but not universal among all genera or species. The exact mechanism of microbiological attack on cellulose is not known, even though considerable information has been accumulated.

Cellulose derivatives substituted at various positions in the molecule were evaluated for resistance to attack by one of the most active cellulolytic fungi—*viz.*, *Myrothecium verrucaria*. Cellulose acetate, containing 9.3% or more acetyl; cellulose triacetate; ethylcellulose, 45.8% ethoxy; methylcellulose, degree of substitution, 2.0; and 6-cyanoethylcellulose, containing 1.7 CN groups per anhydroglucose unit, were found to be completely resistant to attack. Cellulose acetate with 3.4% and 5.1% acetyl, cellulose-6-nitrate, and 6-carboxycellulose were only slightly resistant. Cellobiose octacetate and pentacetyl glucose were completely resistant to the attack of *M. verrucaria*. These data suggest that the resistance of the cellulose molecule to attack by this fungus can be attributed to a chemical blocking of one or more of the alcoholic groups.

Preliminary data on the isolation and properties of a cell-free enzyme preparation from *Myrothecium verrucaria* are presented. There is still need for a considerable amount of additional research on the enzymes of cellulose-decomposing fungi, both as to the nature of the enzymes and their mode of action, as well as on their occurrence in various fungi at different stages of growth.

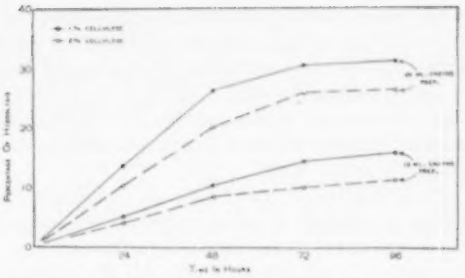

Fig. 4. *The effect of enzyme and substrate concentration on rate of hydrolysis of cellulose. Results are averages for 5 replicates.*

Appendix

A. Method of Determining Alkali Solubility, Fluidity, and Copper Number

1. Alkali Solubility

Cotton was prepared by extracting for 4 hrs. in a Soxhlet extractor with 95% alcohol; 0.1 g. of air-dried cotton was transferred to a pyrex A.O.A.C. titer test tube. The test tube was immersed in a water bath which was controlled at 25°C ± 1°C, and exactly 1 ml. of 10*N* sodium hydroxide solution, previously brought to the temperature of the water bath, was added. The cotton was thoroughly wetted with the aid of a stirring rod and was allowed to stand for 15 min. Then, exactly 4 ml. of distilled water, also previously brought to the same temperature, was added, with immediate stirring. This temperature was maintained for 1 hr., with stirring every 15 min.

The preparation was then filtered through a small Gooch crucible containing an oven-dried mat of prepared, medium asbestos which had been extracted with alkali and acid, according to the Munson and Walker sugar method. Two ml. of the filtrate was pipetted into a pyrex A.O.A.C. titer test tube containing 10 ml. of 0.2*N* potassium dichromate (or 0.5*N* if the cotton is badly deteriorated). The test tube was shaken, stoppered with a 6-in. air condenser made of 8-mm. OD glass tubing, and heated in a glycerin bath at 100°C for 1 hr. The mixture was then

cooled, transferred to a 200-ml. Erlenmeyer flask, and 10 ml. of 95% sulfuric acid, 90 ml. of distilled water, and 2 drops of *o*-phenanthroline indicator (or 7 drops of phenylanthranilic acid indicator) were added. The solution was titrated with 0.1*N* ferrous ammonium sulfate, which had been standardized immediately before use.

From the weight of dichromate consumed, the weight of cellulosic material in the alkaline solution can be calculated on the assumptions that it is represented by the formula $C_6H_{10}O_5$ and that complete oxidation to water and carbon dioxide occurs. One l. of *N* dichromate is equivalent to 6.75 g. of cellulose.

2. Copper Numbers

Copper numbers were determined on 1.5-g. samples of finely divided fibers which had been treated with Braidy's solution and heated for 3 hrs. in an oil bath which was thermostatically controlled at 100°C [1].

3. Fluidity Measurements

Fluidity measurements were made according to the procedure described by Conrad [6].

B. Preparation of Cellulose Triacetate of Varying Degrees of Polymerization

Fifty g. of cotton linters were soaked in glacial acetic acid for several hours at room temperature, freed of excess acid by filtration, and transferred to stoppered glass flasks. The swollen cotton was treated with a mixture of 200 ml. acetic anhydride in 300 ml. of benzene and, after thorough mixing, a few ml. of perchloric acid, disolved in a mixture of the above acetic anhydride-benzene, was added.

The contents of the flasks at the end of 24 hrs. were filtered by suction and subsequently washed with benzene, alcohol, and water. All trace of free acids was carefully removed. The water was displaced with alcohol, and the alcohol with ether, and the cellulose triacetate was dried in air.

The data for the cellulose triacetate follow:

Time of reaction (hrs.)	Perchloric acid content (g.)	Acetyl content (%)*	D. P.
24	0.0735	44.3	390
24	0.9750	45.1	110

* Theoretical value = 44.79%.

C. Preparation of a Polyhomologous Series of Hydrocelluloses

Seventy-five g. of cotton linters were refluxed with 2 l. of 0.25*N* sulfuric acid in a wax bath, the temperature of which was maintained at 140°C. It required 10 to 15 min. for the contents of the reaction flask to reach the boiling temperature. At the desired interval the hydrocellulose preparations were filtered on a Buchner funnel, washed with cold water, and allowed to stand for from 12 to 24 hrs. in cold water or until the supernatant liquor showed neutral reaction to litmus paper. The suspensions were then filtered and the residues were suspended in alcohol for approximately 2 hrs., with occasional stirring. The alcohol was displaced with ether, the ether was sucked off on the Buchner funnel, and the residues were air-dried on filter paper.

D. Preparations of Extracts from *Myrothecium verrucaria* Containing Active Cellulases

After many preliminary experiments the following method was adopted: 100 g. of dewaxed cotton fiber, which had been finely divided in a Wiley mill to pass through an 80-mesh sieve, were weighed into 6-l. Erlenmeyer flasks and autoclaved; 2 l. of a sterile mineral-salts medium, Formula A [16], was added. The flasks were inoculated with 2 ml. of a spore suspension of *M. verrucaria*, USDA No. 1334.2, prepared as described by Greathouse and associates [16]. The flasks were plugged with sterile cotton, and were shaken at the rate of 50 cycles per min. in order to keep the ground cotton in suspension. After 7 days of incubation at 28°C ± 2°C, the cellulose-mycelium pellets were filtered on a Buchner funnel, the filtrate being collected and stored in a refrigerator at from 3°C to 5°C, using toluene as an antiseptic. The cellulose-mycelium pellets were ground with quartz sand and were extracted with the mineral-salts medium. Both filtrates were mixed together and dialyzed against distilled water for 24 hrs. in du Pont cellulose acetate tubing. The filtrate was then concentrated at 2°C *in vacuo* and dialyzed against distilled water for an additional 24 hrs. in order to remove salts and other dializable matter. Since the enzyme preparations were not sufficiently stable, only fresh preparations were used. These preparations had a greater activity and stability than those dialyzed only once.

E. Method of Determining an Index of the Cellulolytic Activity of *Myrothecium verrucaria* Extracts

Into a 250-ml. Erlenmeyer flask, 20 ml. of dialyzed filtrate was added to 30 ml. of phosphate buffer of pH 5.0 and 0.5 g. of dewaxed cotton, Stoneville 2B (either unpulverized entire fibers or fibers which had been pulverized in a ball mill for 48 hrs.). Toluene was added as an antiseptic. After incubation for 24–96 hrs. at 40°C, the mixture was carefully filtered and one or more of the following were determined: (1) the amount of reducing sugars, as determined by the Munson and Walker gravimetric method [1]; (2) loss in weight from the original; (3) decrease in tensile strength, determined by means of the Pressley breaking-strength technique. Each test was checked for possible contamination with microorganisms by means of plating out on nutritive media and observing any growth. Blank controls were run for each experiment.

F. Identification of Reducing Sugars

The filtrate containing an enzyme-cellulose (obtained from ball-milled cotton) was used for identifying glucose according to the Munson-Walker sugar analysis [1]. Results indicated a conversion of 18.0% of the cellulose into reducing sugars (calculated as glucose). The filtrate was reduced by one-tenth in volume by vacuum. The osazone was prepared and purified by recrystallization from 50% ethyl alcohol. The uncorrected melting-point value of the osazone was 199°–201°C. A similar preparation of glucose of known purity gave a melting point of 201°–202°C. These data indicate that the major reducing substance resulting from cellulose hydrolysis was glucose.

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Measurement and Theory of Absorbency of Cotton Fabrics

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Abstract

High and uniform absorbency of cotton fabrics is a desirable quality in nearly every wet-finishing operation and in many finished fabrics; yet absorbency-measuring tests which have been employed up to the present time are largely inadequate and arbitrary. A test method is described here which is more suitable in that it meets the requirements of wetting the fabric quickly from one side while it is under pressure and allowing the comparison of different fabrics in a readily understandable manner.

Using a glass filtering funnel to provide a wet porous plate and a flowmeter for measuring rates, the apparatus is easily assembled and calibrated. The test is simple and rapid and permits numerical evaluation of both rate of absorption and total or ultimate absorption, largely independently of apparatus characteristics. The separate evaluation of these absorbency factors and the elimination of timing procedures set this test apart from those previously published. The method is readily adaptable to the investigation of many liquid-absorbent relationships.

Application of the test to the evaluation of absorbency of purified cotton fabrics has led to a plausible explanation of their absorption behavior as being due largely to spaces within the fabric rather than to absorption characteristics of the fiber itself.

ABSORBENCY in textiles is the quality of taking up a fluid in the manner of a sponge. It is involved in every finishing operation, and is especially troublesome to the textile finisher when it is subject to variation, which may result in nonuniform printing and nonlevel shades in dyeing. Absorbency is a desirable quality in many finished fabrics, especially in those used for underclothing, wash cloths, diapers, towels, napkins, gauze, and bandage materials, and in absorbent cotton. Because this quality of absorbency is significant throughout the textile field, its measurement and evaluation are important. Yet absorbency tests employed thus far are widely recognized as inadequate, often not measuring the property of most importance. They do not meet the requirements of wetting a fabric or other absorbent material quickly from one side while it is under pressure and of allowing comparison of the rates or amounts of absorption for different fabrics in a readily understandable manner.

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Previous Methods

Larose [5] had published in 1942 a method which had the above objective of improved evaluation but which had advanced only one step toward achieving the precise test method desired. In order to measure rates of absorption, weighed pieces of toweling were contacted with damp porous plates for various periods of time and the moisture absorbed was measured and related to time.

Kettering [4], in 1948, at the Southern Regional Research Laboratory, modified the apparatus of Larose by adding a calibrated side-arm as a source of water for the porous plate. Larose's time-consuming operations of weighing were thus replaced by the more convenient operation of timing the passage of a meniscus by the calibration marks of the supply tube. Kettering's method was satisfactory for evaluating relatively the effects of bleaching operations on the absorbency of print cloth.

The principles applied by Kettering are ideally suited to a system in which there would be no external influences such as capillarity of the source tube, roughness of the porous plate, or resistance of the

plate, so that the observed phenomena would be due to the influence of the cloth alone. However, when each of these external influences is minimized, the rapidity of the phenomena increases so that timing becomes a great problem.

One approach is the use of plates of low porosity, but this is feasible only up to the point at which the resistance of the plates becomes so much greater than that of the cloth that the absorption characteristics of the latter become of secondary importance.

Another way of retarding the rate of absorption involves lowering the water-supply level. The absorptive forces are partially counteracted by the difference in levels, the rate of absorption is thus reduced, and more precise data are obtainable. This approach was adopted by Jackson and Roper [3] for the determination of the absorbency of terry toweling. However, retarding forces are not found in normal applications of absorbent materials, and the effect on the results could not be fully evaluated. Relative absorbencies within a group of samples could be obtained, but not absolute ratings reproducible in different laboratories on different apparatus.

These general principles have been applied more extensively and the previously used apparatus has been continually improved at the Southern Regional Research Laboratory. The purpose of this paper is to report in detail the improvements of the test method and the knowledge which has been gained concerning the fundamentals of absorbency of purified cotton fabrics.

Apparatus

The most recently developed apparatus for the testing of water-absorbency of purified fabrics is shown in Figure 1. A filtering funnel, Pyrex #36060-HAXUB,* provides a medium-porosity plate; a float-type flowmeter allows direct observation of the rates of flow; a source tube constitutes a monolevel reservoir; and a bottle holds a supply of water at room temperature. A buret is included for calibrating the source tube and for measuring the total volume of water absorbed when this volume exceeds the calibrated volume of the source tube. In the latter use, the volume required to refill the apparatus is noted.

The flowmeter which is used is a laboratory kit type, with interchangeable metering tubes and floats

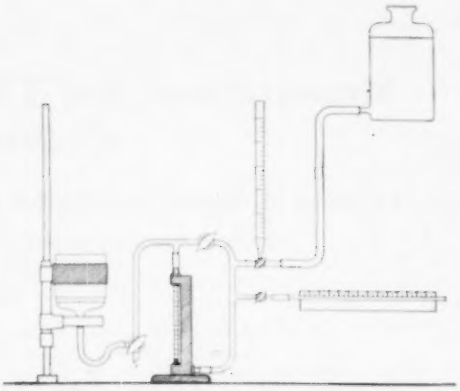

FIG. 1. *Water-absorption testing apparatus.*

to cover the ranges (approximately) 0.1 to 2.7 cc./min. ($\frac{1}{16}$-in. stainless-steel float in 08–150 tube), 1.0 to 18.5 cc./min. ($\frac{3}{32}$-in. glass float in 06–150 tube), and 2.5 to 60 cc./min. (additional $\frac{3}{32}$-in. stainless-steel float for use in 06–150 tube), of the Fischer and Porter Company.*

The source tube consists of 10 ft. of $\frac{1}{2}$-in. (nominal) copper tubing coiled spirally and joined by a rubber connection to 3 ft. of S-coiled 5-mm.-outside diameter glass tubing which is calibrated by filling with measured volumes of water from the buret. The coils are soldered and clamped to a sturdy plane of metal and are handled as a unit.

In operation, the apparatus is filled with water and the stopcocks are set so that any water which passes through the porous plate must come from the source tube. Samples of the fabric to be tested are cut with a circular die of the same diameter as that of the plate and are pressed on the plate by a bag of nonabsorbent material containing 1.0 kg. of fine lead shot. This action causes water to be absorbed by the sample. Suitably shaped nonabsorbent bags may be fabricated of thin films such as 0.004-in. vinyl resin, commonly available for table coverings, or 0.005-in. rubber sheeting, occasionally available from laboratory suppliers as extra-lightweight dental dam. Also used have been lightweight cotton fabric bags with a disc of moistureproof cellophane between bag and sample—the cellophane disc must be replaced for each determination.

For the rating of samples, details of which are given in the Procedure section, no timing operations are necessary. However, for the discussion of absorb-

* The mention of specific products does not imply that they are recommended or endorsed by the Department of Agriculture over similar products not mentioned.

ency relationships it may be assumed that timing is begun at the moment pressure is applied to the cloth against the wet plate.

Absorbency Relationships

The volume of water absorbed can be plotted against elapsed time, as in Figure 2. Since the absorbed volume increased more slowly as it neared the ultimate value, exponential curves were drawn from the origin, fitting best the higher values and the ultimate absorption. Such curves may be represented by the general equation

$$q/Q = 1 - \epsilon^{-tI/Q}, \qquad (1)$$

in which q is the amount absorbed at time t, Q is the ultimate absorption, and I is the initial flow rate, which is theoreticaly the maximum flow rate. Ordinarily, the only data taken are the maximum flow rate and the ultimate absorption, the complete data required for the plotting of curves seldom being noted.

These two factors, maximum flow rate and ultimate absorption, can be evaluated for differences in water levels between zero and 60 cm. with the present laboratory setup. The effective difference in level, or head, is approximately the height of the source tube minus the height of the plate.

Examination of absorption curves obtained with the source tube at various levels below the plate shows that both rate of absorption and ultimate absorption are decreased as the source tube is lowered (see Figure 2). Furthermore, the experimentally determined points deviate widely from the exponential curves, and the maximum flow rate is no longer the initial flow rate. This is the first difficulty when negative heads are used.

A more practical objection to negative heads is evident from Figure 3, which shows the variation of maximum rate of flow with variation in head for three fabrics. (Identifying details and descriptions of all fabrics are given in Table I, which also contains ratings which will be cited throughout this report.) Comparing the maximum rate of flow (column 8) of fabric D with that of fabric B, it is seen that B is superior by a factor of about 3 to 1 at zero head, whereas at − 50 cm. its superiority is nearly 10 to 1. Such observations as this, unfortunately, make the understanding of fabric ratings derived through measurement of absorption rates at negative heads difficult, as was pointed out by Jackson and Roper [3]. Furthermore, the selection of any particular negative head over any other cannot be justified.

By use of the flowmeter and the elimination of timing procedures, true maxima are obtained rather than the lower figures which are derived by calculation from relatively large increments of volume and time [3–5]. Accuracy of the maxima values is verified by the observation that no difference in the maximum is shown whether the float ball is allowed to rise from zero at the start of the experiment or is suspended at a point very near the maximum expected.

The absence of timing difficulties in the newer method also allows the curves to be carried to zero head. When this is done, it is seen that the curves (Figure 3) straighten markedly. Therefore, a line was fitted using the general equation of hyperbolas asymptotic to the zero flow line:

$$Y = a + bXY + cY^2. \qquad (2)$$

Standard deviations [1] are approximately 0.007 cm.^{3}/sec., which is equivalent to less than the scale difference covered by the diameter of the float ball. For this reason the fitted curves only are shown. It is on the basis of the practically linear relationship near zero head that the method of rating which is presented below has been developed.

Figure 4 shows the variation of ultimate absorption of the same samples with variation in head. As with rates of absorption, increasing the negative head decreases the ultimate absorption in a relationship that can also be represented by a section of a hyperbola. One may note, however, an independence of initial rate and ultimate absorption; the order of the samples with respect to ultimate absorption at zero head is different from their order with respect to maximum rate of absorption (Figure 3).

Absorbency Ratings

Absorption curves for three fabrics at zero head (Figure 5) demonstrate that neither the initial rate of absorption (preferred by Kettering), nor the evaluation of the rate over a specified range (preferred by Jackson and Roper), nor the ultimate absorption adequately characterizes the samples as to absorbency. Fabrics E and D have practically identical initial rates of absorption, whereas fabrics E and C have almost the same ultimate absorptions, yet no two of them could be considered alike.

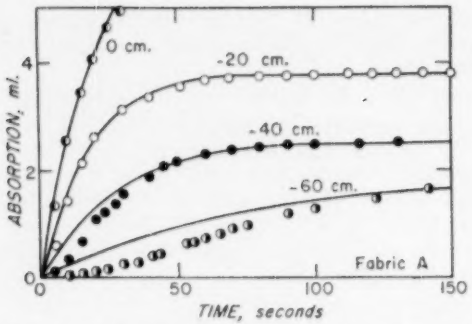

FIG. 2. *Volume absorption curves, with variation in source-tube height.*

In contrast, a rating showing differences among samples by the expression of initial rate of absorption "by" the ultimate absorption (*i.e.*, a two-dimensional figure) does provide a satisfactory statement of absorbency. The magnitude of each factor will increase as the absorbency of the fabric increases. Considering the mathematical product of the factors which comprise the rating of each fabric, the fabrics are arranged in the order C, E, D, with D being the poorest, which is the reasonable order. Although often considered as a product, the factors should always be expressed separately, in as much as fabrics for which the products are equal do not necessarily behave alike. In addition, one of the two factors may be of greater importance in a particular use.

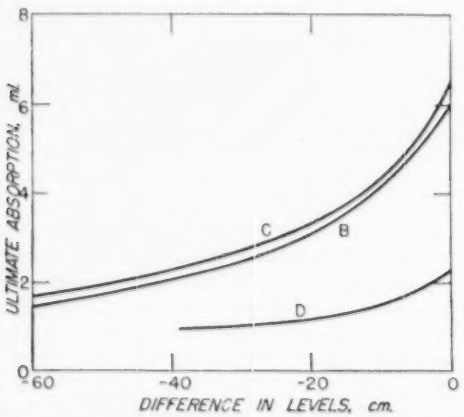

FIG. 4. *Variation of ultimate absorption with variation in head for 3 fabrics.*

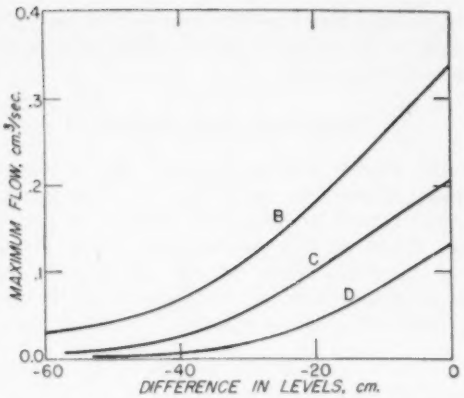

FIG. 3. *Variation of maximum rate of flow with variation in head for 3 fabrics.*

It should be pointed out that Figures 2, 3, and 4 display phenomena which are functions of the porous plate as well as of the fabric sample thereon. For example, whereas fabric D on a medium-porosity plate exhibited a maximum rate of flow of 0.133 cm.³/sec. (Figure 3), on a coarse plate the maximum flow rate was 0.160 cm.³/sec., both observations being made with the source tube at zero height. As long as porous plates in different funnels are not sufficiently alike to permit interchange without affecting the data, direct statements of data will obviously not be satisfactory as absolute ratings.

It is further desirable that each factor be expressed on the bases of zero head, zero resistance, a standard or unit area of sample, and standard textile conditions. These bases are consistent with the usual

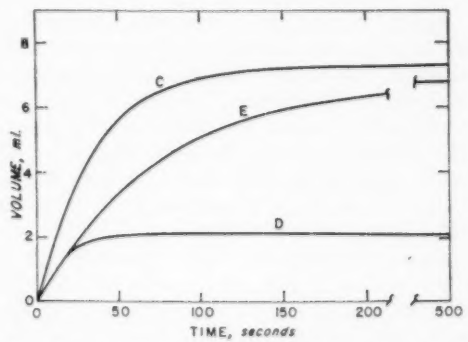

FIG. 5. *Absorption curves for 3 fabrics at zero head.*

TABLE I. Descriptions and Ratings of Fabrics

Fabric designation	Description of fabric	Thread count ($W \times F$)	Let-off ratio of loop threads	Thickness (in.)	Sample weight* (g.)	Delay in reaching max. rate of flow (sec.)	Absorbency rating Max. flow rate (cm.³/sec.)	Absorbency rating Ult. absorption (zero head) (ml.)
A	Terry, white, scoured (otherwise same as C)	—	3.15:1	0.086	2.18	3.8	0.19	7.25
B	Terry, white, scoured	68 × 35	3.55:1	.059	1.72	3.5	1.89	6.05
C	Terry, white, commercial finish (same as A, but not scoured)	87 × 33	3.15:1	.068	2.08	—	.42	6.44
D	Crash, scoured (otherwise same as G)	59 × 37	—	.023	1.00	4.0	.24	2.40
E	Knitted, looped pile face, plain back, tested plain (flat) side to plate	—	2.54:1	.062	1.8	3.6	.20	6.65
F	Knitted (same as E), tested looped side to plate	—	2.54:1	.062	1.8	4.6	.14	6.74
G	Crash, commercial finish (same as D, but not scoured)	59 × 35	—	.018	—	—	.014†	1.18
H	Crash (same as G, but home-laundered 20×)	59 × 40	—	.020	1.06	—	.19†	1.97
J	Crash, mercerized	—	—	—	—	—	.006†	0.58
K	Crash, mercerized, home-laundered 20×	64 × 46	—	.024	1.36	—	.16†	1.99

* Circular sample, 51.4 cm.²

† Uncorrected for effect of porous-plate resistance.

mode of application of absorbent materials and would be understood readily. Toward this end, a mathematical treatment has been devised which eliminates the effect of the plate resistance, so that plates of equal resistance are not necessary for the duplication of absorbency ratings.

The present authors prefer expression of the amount of water absorbed rather than a percentage figure, since, logically, a sample which absorbs at twice the rate, or twice the volume, for a given area would be judged the better absorbent medium by a user. And, as will be explained, there is not necessarily any relationship between sample weight and absorbency. It is recognized, however, that a percentage figure based on sample weight might be valuable in some circumstances, and, accordingly, sample weights (column 6) are included in Table I.

If the contact pressure is too low, grossly nonuniform wetting occurs. The pressure at which this begins to be noticeable depends upon the texture of the cloth. Since terry toweling, likely to be the worst offender, wets satisfactorily at 17 g./cm.², a contact pressure slightly greater, 20 g./cm.², was selected for the method.

At least one important factor remains to be investigated—the manner of eliminating the effects on the ratings of roughness of the upper surface of the plate. The fact that the roughness of the plate cannot be specified independently of its resistance complicates the matter by making it impossible to isolate the effects. However, results have been encouragingly consistent in this laboratory over a period of 1 year using one particular funnel, the plate of which has suffered a change in apparent resistance from 120 to 80 sec./cm.²

Procedure

There are many details incident to the operation of the various absorption testing apparatus using the principles applied here which have been omitted in the interest of brevity. Jackson and Roper [3] have listed many of these and discussed the effects of many laboratory variables which are of importance.

Flowmeter Calibration

It was found necessary to calibrate individually each combination of float and tube used in the flowmeter. This may be done by passing water at a

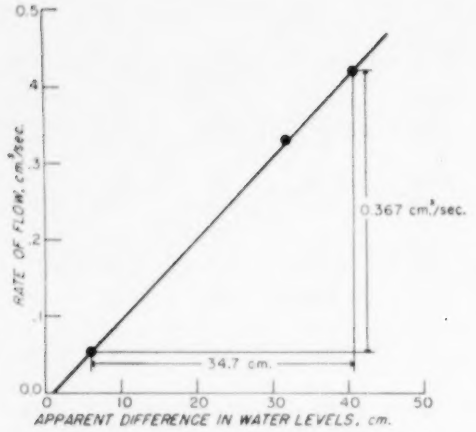

FIG. 6. *Plot of porous-plate calibration data.*

constant rate through the meter, collecting the effluent for a known period, and weighing. For the most accurate results, the temperature of the water should also be maintained constant and correction should be made for the density.

Plate-Resistance Determination

With the apparatus assembled, the particular porous plate to be used must be calibrated—that is, its resistance must be determined. This is done by raising the source tube above the level of the porous plate and observing the rate of flow of water through the flowmeter, and therefore through the plate, for different heads. The upper surface of the plate and the plane to which the source tube is secured are convenient index levels for measurement. Typical data obtained with a medium-porosity plate are shown in Table II. The observed rates of flow are plotted against differences in water level in Figure 6, giving a straight line.

The general equation for this straight line may be written, in this instance, as

$$E = RI + e, \tag{3}$$

where E is the height of the source tube, R is the resistance of the plate, I is the rate of flow, and e is the height of water in the funnel. This equation holds true for the porous plates over the range of flow rates in these experiments, as proved by the straight line (Figure 6). The resistance of the

TABLE II. CALIBRATION DATA FOR PLATE NO. 1 (MEDIUM POROSITY)

Positive head (cm.)	Rate of flow (cm.³/sec.)
6.0	0.053
31.9	0.33
40.7	0.42

plate, R, can be evaluated without absolute measurements of heights since, for practical purposes, the height of water in the funnel may be fixed, and

$$R = \frac{\Delta E}{\Delta I}. \tag{4}$$

Using the data given in Table II,

$$\text{Resistance of plate} = \frac{(40.7 - 6.0)\text{ cm.}}{(0.42 - 0.053)\text{ cm.}^3/\text{sec.}} = 94.6\text{ sec./cm.}^2 \tag{5}$$

The intercept of the plotted line with the axis representing zero flow gives the height of the source tube, or, more precisely, the height of the index line on the source-tube assembly, corresponding to zero effective head. It is found that for zero effective head, the source tube must be placed above the plate to compensate for the capillary force of the small tubing employed. In the instance being cited, the exact value is 0.9 cm., which of course is valid only for the particular combination of funnel and source tube used. Appropriate similar correction has been made throughout this report, except in Table II and Figure 6.

In the determination of plate resistance, the value obtained includes the resistance of the supply lines and the source tube as well as that of the plate. In practice, as the water is removed from the source tube during the calibration, the total resistance of the system decreases. If the resistance of the plate is low, or if the flow rate being used for the determination is high, the rate of flow increases as the experiment proceeds. For this reason, each flow reading should be taken with the source tube as nearly full as possible.

In order to maintain constant resistance, certain precautions should be observed in the handling of the porous plate. It must be thoroughly wet, free of entrapped air, and, once this condition is satisfied, the plate should not be dried. It is cleaned in hot sulfuric acid containing 10% nitric acid, since this

reagent is easier to make than chromic acid, is easily replenished as the nitric acid is used or vaporized, and it cannot deposit solids within the plate if allowed to exhaust itself. The plate is washed first by rinsing in distilled water a few times and then by aspirating distilled water through it for an hour or so. When assembled into the apparatus, it is covered with an inch or so of water when not in use. There is also some advantage in using 0.1% benzoic acid throughout the apparatus instead of pure water —this reduces microbiological growth, yet the surface tension of the solution is not appreciably affected.

Rate of Absorption

To rate a fabric, a number of discs are cut to fit the porous plate. Successive runs are made with the source tube at zero level and at -6 and -12 cm., observations being made of maximum rates of flow and ultimate absorption, the latter at zero head only. Since over this range the relationship between flow and head is linear, zero and one other level would be satisfactory, but as a check it may be preferable to make determinations at three levels, as is shown in Table III. These averages have been derived from 10 determinations for each point, but 5 are often satisfactory. The data are plotted in Figure 7.

As in equation (4), the ratio of change in head to change in flow is obtained, the quotient representing the summation of plate resistance plus the resistance of the cloth to wetting. In this case,

$$R_{\text{cloth + plate}} = \frac{6.0 \text{ cm.}}{0.032 \text{ cm.}^3/\text{sec.}} = 188 \text{ sec./cm.}^2. \quad (6)$$

If the value previously found for the resistance of the plate alone is subtracted, the difference is the resistance of the cloth alone to wetting:

$$R_{\text{cloth alone}} = 188 - 94.6 = 93 \text{ sec./cm.}^2. \quad (7)$$

From equation (3), by simultaneous equations, it follows that, for a constant head, flow is inversely proportional to resistance, or

$$R_1 I_1 = R_2 I_2, \quad (8)$$

E and e being held constant. Knowing the resistance of the cloth plus that of the plate, R_1, the flow at zero head when the cloth and plate are present, I_1, and the resistance of the cloth alone, R_2, the flow which would be obtained at zero head if the cloth alone was acting, I_2, is readily obtained by proportion:

$$\text{Max. rate of flow, cloth alone} = \frac{0.207 \times 188}{93} = 0.42 \text{ cm.}^3/\text{sec.} \quad (9)$$

A seeming difficulty occasionally appears in these calculations. With samples of very low resistance to wetting, inadequate sampling or small errors in observation lead to erroneous results due to the evaluation of small differences between large numbers in equation (7).

For routine, all of the mathematical operations can be combined into one equation, allowing solution for the absorbency rating without plotting. A convenient expression is

$$I_2 = \frac{h_1 I_1}{h_1 + R(I_1 - i_1)}, \quad (10)$$

TABLE III. WATER-ABSORPTION DATA FOR FABRIC C

Negative head (cm.)	Average max. rate of flow (cm.³/sec.)	Average total absorption (ml.)
0	0.207	6.44
6	0.175	—
12	0.144	—

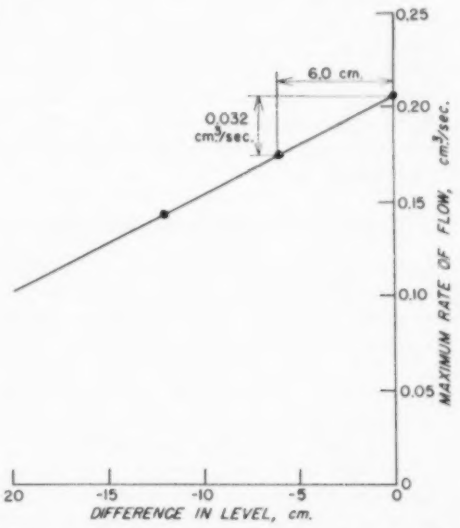

FIG. 7. *Plot of water-absorption data for fabric C.*

FIG. 8. *Schematic drawing of cross sections of fabrics in contact with a porous plate.*

in which h_1 is the head other than zero chosen for the determination and i_1 is the maximum rate of flow observed at that head. For the data given in Table III:

Max. rate of flow, cloth alone

$$= \frac{-6.0 \times 0.207}{-6.0 + 94.6(0.207 - 0.175)} \qquad (11)$$

$$= 0.42 \text{ cm.}^3/\text{sec.}$$

Ultimate Absorption

No calculation is needed to obtain a figure for the ultimate absorption which would be obtained with a porous plate of zero resistance in as much as the resistance of the plate has no effect on the volume ultimately absorbed. Therefore, the ultimate absorption observed at zero head, which in this example is 6.44 ml., is reported directly.

Final Statement

The absorbency rating of the sample is expressed by 0.42×6.44 for a 51.4-sq.-cm. sample. These figures are the rate of flow and the ultimate absorption which would be exhibited by the sample under no retarding influences. Alternatively, the rating could be expressed in terms of unit area, but reduction to a basis of 1 sq. cm. results in inconveniently small numbers.

Theory of the Absorption Mechanism

Various phenomena have appeared in this investigation which have led to a plausible theory of absorption mechanism. Cross sections of fabrics in contact with porous plates are shown schematically in Figure 8. The surface of the plate is the termination of many capillary channels which flare outward (but still remain of capillary size) to meet adjacent channels. The water rises along each capillary wall to the upper limit of the wall, where it meets the liquid at the upper limits of the adjacent capillaries. The columns of water, meeting thus, merge to form a continuous wet surface.

There are three primary phenomena (represented in Figure 2) which a theory of absorption mechanism must explain: (1) time lag; (2) rate of absorption; (3) ultimate absorption.

The time lag is the initial period during which no significant volume of liquid is absorbed. Decreasing the negative head reduces the lag, but a slight delay is evident in larger-scale plots even at zero head.

Unless the contact pressure of the cloth against the porous plate is very great, the fabric is initially wetted only at the cross-over points of the yarns, where it is thickest. At these points, the water is drawn into the fiber bundle, the interfiber spaces filling rapidly. Because of the small volume of these spaces, however, the rate of absorption is quite small. As interfiber absorption continues, the walls of the interyarn spaces become wet, and these spaces, too, can be filled by capillary action. This marks the beginning of significant flow. Of course, these actions are progressing concurrently—that is, in one area of the sample interyarn absorption is progressing while in another area this action is still waiting upon the interfiber action. As successively greater amounts of water drawn into the cloth wet more and more interyarn wall surface, the volume effect rapidly increases.

The rate of absorption has been defined as the ratio of absorptive forces to the resistance of the fabric to wetting, by equation (3) which, upon elimination of error and subsequent rearrangement, yields

$$I = E/R. \qquad (12)$$

In considering rates, the writers have placed emphasis on the maximum rate. A suitable explanation of absorption must include identification of the rate-determining factors.

The resistance, R, is the resistance to wetting centered in the initial contact areas, since all of the water entering the fabric must pass through them. This resistance is not the same as that offered by a wet cloth to water being forced through it, in which case the paths through the interyarn spaces offer much less resistance. This has been confirmed by Jackson [2]. A cloth with a resistance to wetting of 70 sec./cm.^{2} was found to have a resistance of only 2 to 3 sec./cm.^{2} to the transmission of water when wet.

Loops on fabrics such as terry and certain knitted constructions emphasize the idea of contact points

and their associated resistance. Two absorption ratings obtained on one fabric which has loops on one side only are given in Table I. The rating of fabric E, for the plain or flat side of the fabric against the plate, shows that contact is better and resistance to wetting is lower because the maximum rate of flow is greater by 36% than that obtained with the looped side against the plate (fabric F).

The absorptive force, E, may be evaluated by extension of the tangents to the curves relating maximum rate of flow and head (Figure 3) to interception with the zero flow axis. The intercept of fabric C shows that an external head of -40 cm. of water would be sufficient to reduce the maximum flow rate to zero. If it is assumed that capillary action is being counteracted, the effective capillary radius can be evaluated at 0.004 cm. from the surface tension equation

$$\gamma = hdgr/2. \qquad (13)$$

The significance of this capillary radius is more apparent after consideration of the next phenomenon.

The third phenomenon to be considered is ultimate absorption. The relationship of ultimate absorption to head permits an additional evaluation of the absorptive forces. In Figure 4 it may be seen that if the ultimate absorption of fabric C continued to decrease with increasing negative head at the same rate as that observed in the neighborhood of zero head, a negative head of 20 cm. of water would be sufficient to prevent absorption. The corresponding force in the fabric can reasonably be attributed to the action of capillary channels within it. From the 20-cm. value, the effective capillary radius at zero head is calculated to be 0.007 cm. Study of photomicrographs of cotton fabrics shows this to be the order of magnitude of the interyarn spaces.

Each of these two calculations evaluates the average radius of the same capillary channels, the sizes and shapes of which differ over a wide range. Their agreement is satisfactory considering the nature and the independence of the two phenomena used. The value derived from the consideration of maximum rates is smaller, indicating that this phenomenon may be disproportionately affected by the cusped cross section of the channels. And, of course, practically all channels contribute to ultimate absorption, whereas only the smaller ones are effective in the initial phase of absorption, in which the maximum rate is observed.

Factors in Laundering

The improvement in absorbency of a fabric upon laundering is readily evaluated by the new test, as illustrated by the data on fabrics G, H, J, and K (Table I). Before laundering, the initial rates of absorption and ultimate absorptions of these fabrics (G and J) varied by a factor of more than 2 to 1. Repeated home launderings (about 20) improved both the rate of absorption and ultimate absorption, the rates being improved more than 10 to 1 (column 8). More significant is that the differences between the samples were evened out, so that after laundering their absorbency behavior became practically identical. Larose [5] noted the same effect when comparing undyed towels with the same constructions dyed by different procedures. Samples which initially varied by as much as 6 to 1 in rate of absorption could not be differentiated after laundering.

This leveling is reasonable within the absorption mechanism proposed, by which absorption is a function of the spaces in the fabric and is not related directly to the quantity of cotton. Accordingly, laundering is principally a mechanical treatment which redistributes the yarns and fibers more uniformly throughout the space available. Thus, for a given construction, fabrics of the same weight become practically identical in absorbency properties after laundering.

Since laundering reduces the size of the larger spaces and increases the size of the smaller ones, there is less waiting of the larger capillary spaces on the filling of smaller ones, all tending to be filled simultaneously, the delay being less, and the maximum flow rate increasing. Whether or not ultimate absorption changes with laundering depends upon the construction of the fabric. In a very open fabric, some spaces are too large to fill completely, whereas after laundering they are small enough to fill. Conversely, if the spaces are all small enough to begin with, the total space available and the ultimate absorption remain the same. In some exceptional constructions, there are very large spaces which do not fill completely even after laundering. If such a sample is wetted by immersion and then subjected to the same pressure and other conditions used in the porous-plate technique, the observed ultimate absorption is greater than that found by the porous-plate method. The ratio of the ultimate absorption values found by these two procedures is about 2:1, or more,

for the looped fabrics, and 1.1 : 1, or less, for flat constructions such as crash.

Extension of Method

The test method is limited neither to the use of pure water in the rating nor to the relatively well-purified cotton fabrics used in the present experiments. In fact, preliminary work has been carried out with the apparatus filled with nonaqueous liquids of low surface tension for the rating of fabrics which do not readily wet with pure water. The results were successful in that flow rates and ultimate absorptions of the same magnitude as those for purified fabrics were obtained. However, the significance of these results is not yet fully apparent.

Jackson and Roper [3] have indicated the sources of many errors in this type of test method. Other sources of error may become significant when this method is applied to unpurified samples or when nonaqueous liquids are employed. In addition to the readily anticipated surface tension and secondary effects, the interfacial situation becomes quite complex if the cellulose has an initial moisture content. And, of course, the calibration of the type of flowmeter used here is different for the different liquids passing through it.

The test method is also adaptable to the rating of wetting and rewetting agents in their effect on lag and rate of absorption, and also to the rating of fabrics for absorption of oils and other liquids which textile materials are often called upon to absorb.

Summary

A simple and rapid test, with apparatus which is easy to assemble, which evaluates numerically two absorbency factors—rate and ultimate absorption—largely independently of apparatus characteristics, is presented. The separate evaluation of these independent factors and the elimination of timing procedures sets this test apart from previous tests. The ratings are more explicit and easily comprehensible.

The test method is readily adaptable to the investigation of many liquid-absorbent relationships and is suitable for application in problems of textile manufacture and finishing. Evaluation in detail of the effects of construction variables may indicate improved absorbent-fabric constructions.

Applications of the test to the evaluation of absorbency of purified cotton fabrics have led to a plausible explanation of absorption phenomena which is based largely on the spaces within the fabric rather than on the fabric itself.

Acknowledgments

Thanks are extended to Miss Mary Rollins for her aid in the interpretation of many photomicrographic sections made under her supervision, and to Mr. Cecil Daul for sample fabrics G, H, J, and K. Other samples were furnished through the kindness of Dr. Raphael Rupp and Mr. E. C. Jackson of the Pacific Mills and of Mr. Lee Tillery of the West Point Manufacturing Company.

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Law of Critical Yarn Diameter and Twist
Influence on Yarn Characteristics*

Alberto Barella †

Abstract

The effect of increased twist upon yarn density is explored and a law of critical diameter is postulated. It is suggested that at the time at which a yarn breaks under tensile load the density of the yarn is equal to the fiber density.

The influence of twist on contraction is examined and prediction formulas are given for cotton, woolen, worsted, and rayon yarns.

THE INFLUENCE and application of the diameter factor and the effect of twist on the diameter, contraction, and other characteristics of yarns are old problems, but about which relatively little is known. Several textile research workers have studied the subject, including M. C. Besset and T. E. Federico López-Amo, and have published helpful and interesting results. The purpose of this work is to discuss these factors and their application to the physical characteristics of cotton, worsted, woolen, and rayon yarns.

Experimental Procedure

Measurement of the diameter of the yarns was accomplished by projecting the magnified image of the yarn on a screen. The yarn was led from the bobbin through an adjustable tensioning device and passed through a tensiometer which indicated the tension at the time of movement. From the tensiometer the yarn was passed through the optical system formed by a projection microscope. Measurement on the screen was effected by means of a scale graduated in half millimeters. The magnifications used depended on the diameter of the yarn and were of the order of 50 to 100. Error of measurement was calculated to be less than 2.5%. For every projection the two maximum and the two minimum diameters were measured. Twenty projections per bobbin were taken on yarn spaced several meters apart. All measurements were made under standard conditions of humidity and temperature.

The fiber density values, taken from data of other authors, are those which are generally accepted.

Two testers were used for the determination of the twist: one, working on the Laisnez principle, accommodates a length of 50 centimeters; the other is a simple untwisting device which handles a length of 10 cm.

The materials studied were yarns of wool, worsted, filament rayon, cotton, silk, and spun rayon.

Law of Critical Diameter

The first consideration is the derivation of a formula for the calculation of yarn diameter.

The weight in g., W, of a meter length of yarn is

$$W = \frac{\pi d^2 \gamma'}{4}, \qquad (1)$$

where d is the diameter of the cross section and γ' is the yarn density.

The weight in g. of a meter length of yarn in terms of the direct metric number kg./m., N', is

$$W = \frac{N'}{1000}. \qquad (2)$$

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Equalizing equations (1) and (2) and solving for diameter,

$$d = 2\sqrt{\frac{N'}{1000\pi\gamma'}}. \tag{3}$$

The value of the yarn density is always lower than that of the fiber, owing to the presence of air spaces between the fibers in a yarn. Values of fiber densities which are generally accepted as correct can be found in reference books, but the yarn densities have not been widely studied.

When calculating the yarn diameter using the fiber density, the value obtained is lower than that obtained experimentally. We call the yarn diameter value obtained by using the fiber density value the "critical diameter."

The law of critical diameter may be defined as follows: If there is no slippage of fibers in a yarn when it is subjected to load, the break occurs when the yarn diameter becomes critical. In this case the yarn density equals the fiber density.

The equation for the critical diameter, d_c, is;

$$d_c = d_0 - K\sqrt{F_R}, \tag{4}$$

where F_R is the breaking load in g. and d_0 is the yarn diameter at zero load.

The general equation is

$$d_f = d_0 - K\sqrt{F}, \tag{4'}$$

where d_f is the diameter under a load of F g. (See Figure 1.)

Equation (4') for d_f, which has been tested experimentally, is true for all classes of fibers and yarns tested. The single variable is coefficient K, which depends upon the fiber and yarn characteristics. Table I shows analytical and experimental results on some filament and spun rayon yarns, and some woolen and worsted yarns. The results are plotted in Figures 2, 3, 4, 5, and 6.

According to the law of critical diameter, d_c can also be calculated from fiber density as

$$d_c = 2\sqrt{\frac{N'}{1000\pi\gamma}}, \tag{5}$$

where γ is the fiber density.

Substituting equation (3) into equation (4) and setting (4) equal to (5), the following equation is

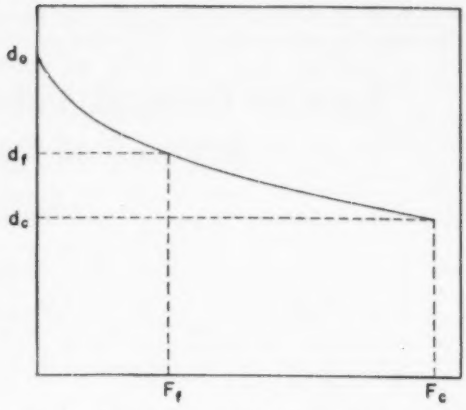

FIG. 1. *General relationship between diameter and tensile load.*

obtained for the coefficient K:

$$K = \frac{2\left(\sqrt{\frac{N'}{1000\pi\gamma'}} - \sqrt{\frac{N'}{1000\pi\gamma}}\right)}{\sqrt{F_R}}, \tag{6}$$

or

$$K = \frac{2\left(\sqrt{\frac{1}{\pi\gamma'}} - \sqrt{\frac{1}{\pi\gamma}}\right)}{\sqrt{1000L}}, \tag{7}$$

where L is the breaking length in km.

The value of K in the case of yarns without dressing (size) is not easily established mathematically; recourse to experimentation has been found necessary in a number of cases. On the other hand, coefficient K is calculated from equation (7) if the breaking length is known.

This means that K depends upon the twist (which affects yarn density), fiber density, and breaking length.

This coefficient K is called the coefficient of diameter of the yarn submitted to strain and it is applied to equation (4') for all values of load, assuming that there is no fiber slippage.

As illustrations of the use of the law of critical diameter, two examples follow.

Example 1:

Yarn: filament rayon

Yarn no.: 100 den. = 90 indirect metric no. (N) m./g. (or km./kg.)

TABLE I. RELATIONSHIP OF YARN DIAMETER IN MM. TO TENSILE LOAD
(COMPARISON OF ANALYTICAL AND EXPERIMENTAL RESULTS)

Yarn	Twist	Test	Load in grams 0	25	50	75	100	125
(K = 0.0038)								
Rayon 100 den.	Normal	Anal.	0.150	0.131	0.123	0.116		
		Exp.	0.150	0.131	0.124	0.118		
Rayon 150 den.	Normal	Anal.	0.175	0.156	0.148	0.141		
		Exp.	0.175	0.157	0.147	0.141		
Rayon 200 den.	Normal	Anal.	0.213	0.194	0.186	0.179		
		Exp.	0.213	0.191	0.186	0.179		
(K = 0.0022)								
Rayon 100 den.	Crepe	Anal.	0.121	0.110	0.106	0.102	0.099	
		Exp.	0.121	0.110	0.105	0.102	0.098	
Rayon 150 den.	Crepe	Anal.	0.148	0.137	0.133	0.129	0.126	
		Exp.	0.147	0.137	0.134	0.131	0.128	
Rayon 200 den.	Crepe	Anal.	0.171	0.160	0.156	0.152	0.149	
		Exp.	0.171	0.161	0.156	0.152	0.147	
Rayon 300 den.	Crepe	Anal.	0.210	0.199	0.195	0.192	0.188	0.185
		Exp.	0.209	0.199	0.193	0.191	0.188	0.186
Spun rayon with dressing (K = 0.0031)								
30s		Anal.	0.214	0.199	0.192	0.187	0.183	
		Exp.	0.213	0.196	0.192	0.186	0.182	
40s		Anal.	0.184	0.169	0.162	0.158		
		Exp.	0.184	0.168	0.162	0.156		
60s		Anal.	0.148	0.136	0.129	0.125	0.120	
		Exp.	0.148	0.137	0.131	0.127	0.122	
Spun rayon without dressing (K = 0.0055)								
30s		Anal.	0.214	0.187	0.175	0.167	0.159	
		Exp.	0.214	0.186	0.174	0.167	0.159	
40s		Anal.	0.184	0.157	0.145	0.137	0.129	
		Exp.	0.184	0.160	0.144	0.137	0.129	
60s		Anal.	0.148	0.124	0.112	0.104		
		Exp.	0.149	0.123	0.114	0.105		
Worsted	T (Twist coeff.)							
50s	95	Anal.	0.172		0.135			
		Exp.	0.169		0.139			
30s	110	Anal.	0.218		0.186	0.179	0.173	
		Exp.	0.217		0.185	0.180	0.175	
30s with dressing	110	Anal.	0.218		0.192	0.186	0.181	
		Exp.	0.218		0.195	0.185	0.181	
35s Crepe	220	Anal.	0.186		0.169	0.165	0.162	
		Exp.	0.186		0.169	0.164	0.162	
Woolen								
10.5s	135	Anal.	0.384		0.351	0.343	0.337	
		Exp.	0.385		0.349	0.344	0.337	
10.5s with dressing	135	Anal.	0.384		0.351	0.344	0.337	
		Exp.	0.385		0.350	0.345	0.338	
12.5s	110	Anal.	0.373		0.338	0.330	0.323	
		Exp.	0.372		0.340	0.329	0.324	

NOTE: By "analytical" is meant "theoretical."

Twist: normal
Tenacity: 2 g./den.
Fiber density (γ): 1.52
Experimental diameter: 0.152 mm.
Breaking length:

$$L = \frac{F_R N}{1000} = \frac{200 \times 90}{1000} = 18 \text{ km.}$$

Critical diameter using fiber density is:

$$d_c = 2\sqrt{\frac{1}{\pi \times 90 \times 1.52}} = 0.0965 \text{ mm.}$$

The yarn density is found by the formula:

$$\gamma' = \frac{4}{\pi \times 90 \times 0.152^2} = 0.639.$$

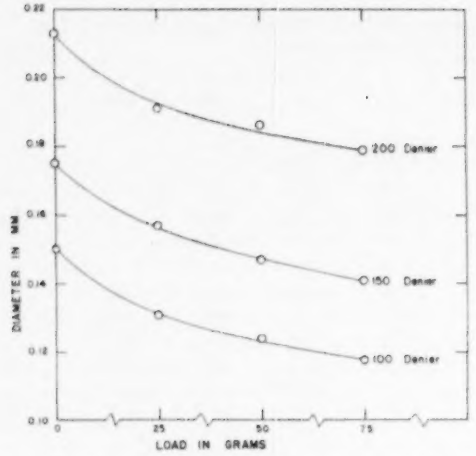

FIG. 2. *Relationship of yarn diameter to tensile load (comparison of experimental results).*

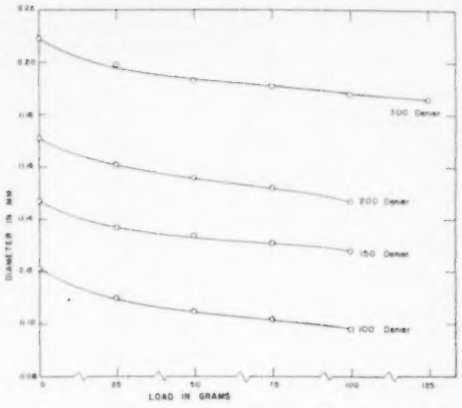

FIG. 3. *Relationship of yarn diameter to tensile load (comparison of experimental results).*

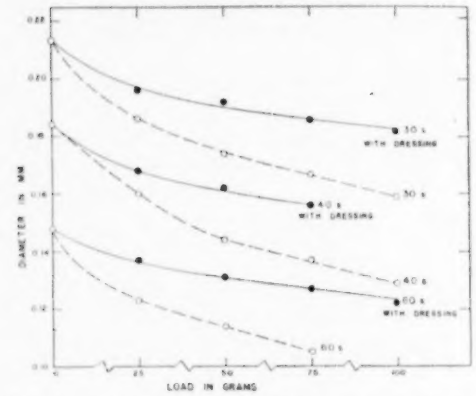

FIG. 4. *Relationship of yarn diameter to tensile load (comparison of experimental results).*

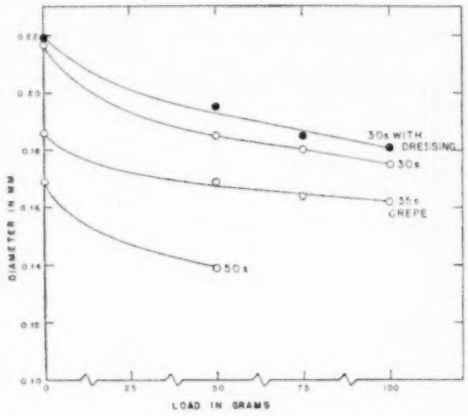

FIG. 5. *Relationship of yarn diameter to tensile load (comparison of experimental results).*

The value K is calculated as:

$$K = \frac{2\left(\sqrt{\frac{1}{\pi \times 0.639}} - \sqrt{\frac{1}{\pi \times 1.52}}\right)}{\sqrt{1000 \times 18}} = 0.00389.$$

Then by substitution into

$$d_c = d_0 - K\sqrt{F_R},$$

where F_R is the breaking strength in g.,

$$d_c = 0.152 - 0.00389\sqrt{200} = 0.0965 \text{ mm}.$$

This coincides with the critical diameter previously calculated.

Example 2:

Yarn: worsted with dressing
Yarn no.: 30 km./kg. (or m./g.) (N)

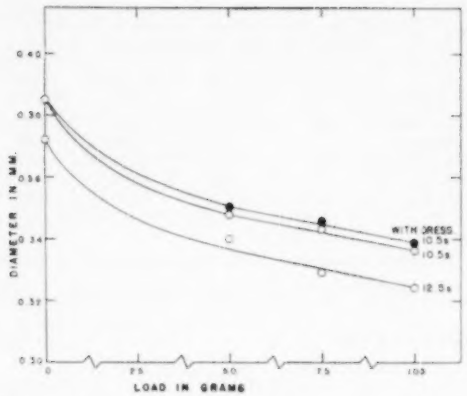

FIG. 6. *Relationship of yarn diameter to tensile load (comparison of experimental results).*

Twist: warp
Experimental diameter: 0.218 mm.
Fiber density: 1.32
Breaking length: 3.45 km.

Critical diameter:

$$d_c = 2\sqrt{\frac{1}{\pi \times 30 \times 1.32}} = 0.179 \text{ mm.}$$

Yarn density:

$$\gamma' = \frac{4}{\pi \times 30 \times 0.218} = 0.893.$$

Coefficient K:

$$K = \frac{2\left(\sqrt{\frac{1}{\pi \times 0.89}} - \sqrt{\frac{1}{\pi \times 1.32}}\right)}{\sqrt{1000 \times 3.45}} = 0.00362.$$

Critical diameter:

$$d_c = d_0 - K\sqrt{F_R}$$
$$= 0.218 - 0.00362\sqrt{115} = 0.179 \text{ mm.}$$

Thus, the value obtained by using equation (4) coincides with that calculated from equation (5).

These results substantiate the concept of the law of critical diameter. The yarn break occurs when the yarn and fiber densities become equal; the inter-fiber spaces theoretically disappear and the yarn acquires a totally compact structure at break if there is no fiber slippage.

The second important consideration is that of the critical diameter's relation to the twist limit and the twist coefficient.

Twist Influence on Yarn Characteristics

The relationship between the yarn density and the twist coefficient for woolen and worsted yarns with normal values of twist (coefficient of 60 to 230) were studied and the equation for this relationship was found to be of linear form:

$$\gamma' = a + bT, \tag{8}$$

where T is the twist coefficient of the original yarn and is equal to twist per m. divided by $\sqrt{N}$; and γ' is the density of the final (twist) yarn.

Twisting influences not only the density factor but also the count of the yarn, through contraction.

As is known, the analytical study of the twist coincides with the geometry of the spirals. All the investigators refer to one spiral, representing the average spiral of those formed by the fibers when twisted. The diameter of this spiral is lower than the yarn diameter, but there is no agreement in the relationship between these diameters.

In Besset's report [1] the influence of twist on the length of cotton yarn is discussed. The author, by analytical means, arrives at the equation for contraction. Another discussion on the subject is a report by López-Amo [2].

The equation derived by Besset is:

$$C = 100\left(1 - \frac{1}{\sqrt{1 + \tan^2\theta}}\right), \tag{9}$$

where C is the percent contraction and θ is the angle formed by the spirals with the axis of the yarn.

The relationship between the twist angle, turns per unit length, and spiral diameter is:

$$\tan\theta = \pi d_t t, \tag{10}$$

where d_t is the diameter of the average spiral and t is the twist per unit length.

For the calculation of $\tan\theta$, Besset considered the average spiral diameter to be equal to one-half the yarn diameter:

$$\tan\theta = \pi \frac{d}{2} t,$$

where d is the diameter of yarn in cm.

In terms of yarn density:

$$\tan^2\theta = \frac{\pi T_1^2}{100\gamma'},$$

where T_1 is the coefficient of twist for turns per cm.

For cotton yarn, which has a yarn density of 0.56, the formula for contraction becomes:

$$C = 100\left(1 - \frac{1}{\sqrt{1 + 0.05T_1^2}}\right). \quad (11)$$

Besset's value of 0.56 for cotton yarn density is lower than the value found for warp yarns (0.83).

Citing some practical examples, Besset states that contraction is influenced only by the twist, and that it is independent of the yarn count.

As seen in Figure 7, the line ($\gamma' = a + bT$) which represents the relationship between yarn density and twist coefficient cuts the ordinate axis at a. This point theoretically represents the yarn density of a yarn with no twist. This value is called the "initial yarn density" and is the same as that taken by Besset as a basis for calculating contraction.

Researchers disagree as to the value of d_t as related to d. For cotton Besset gives $d_t = 0.5d$, while for rayon López-Amo gives $d_t = 0.66d$. Actually, the value varies with different fibers.

The following relationships for yarn densities have been found:

$$\text{Cotton} \quad \gamma' = 0.56 + 28 \times 10^{-4}T. \quad (12)$$

$$\text{Worsted} \quad \gamma' = 0.58 + 25 \times 10^{-4}T. \quad (13)$$

$$\text{Woolen} \quad \gamma' = 0.47 + 28 \times 10^{-4}T. \quad (14)$$

$$\text{Rayon} \quad \gamma' = 0.60 + 27 \times 10^{-4}T. \quad (15)$$

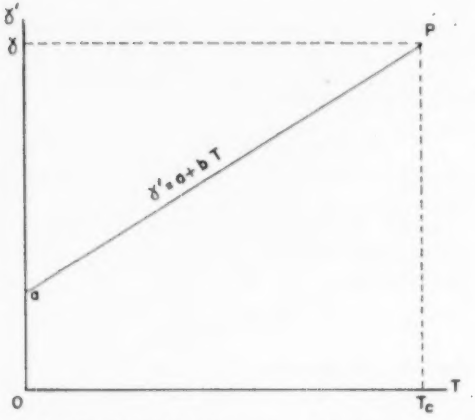

FIG. 7. *Relationship between yarn density and twist coefficient.*

TABLE II. RELATIONSHIP BETWEEN TWIST COEFFICIENT AND YARN DENSITY

Yarn	N	Twist coeff.	Diameter (mm.)	Yarn density
Worsted	50s	95	0.169	0.86
Worsted	30s	110	0.217	0.89
Worsted	35s	220	0.186	1.11
Woolen	12.5s	100	0.371	0.74
Woolen	10.5s	135	0.383	0.83

In these equations T is the coefficient of twist $\left(\frac{\text{turns per m.}}{\sqrt{N}}\right)$. The relationship between twist coefficients used is:

$$T_1^2 = T^2 \times 10^{-4},$$

where $T_1 = \frac{\text{turns per cm.}}{\sqrt{N}}$.

Tests were made on some worsted and woolen yarns in order to find the relationship between twist coefficient and yarn density. Table II shows the results of these tests. From these and other data Figure 8 was constructed. The twist coefficients were calculated from the original yarn count, whereas the density was calculated from the final count after correction for contraction.

In Figure 8 the lines plotted for woolen and worsted cut each other at point P ($T = 300$), where the yarn density coincides with the fiber density. At this point P the air spaces would disappear and the yarn would be absolutely compact.

Because the densities are theoretically equal at point P, there must be a relationship between this point and the critical diameter when a yarn is submitted to a breaking load. For this reason it was suspected that a relationship existed between point P and the twist limit. The following investigation was made.

Case A:

A 50-cm. length of worsted yarn made with crepe twist was fastened in the twist tester. Twist was inserted, without allowing contraction, until the yarn broke. The results of three tests are given below:

Yarn	N	Initial T	Initial tension (g.)	Initial C (%)	Twist per mm. at break	T at break
Worsted crepe	35	230	20	8	1.721	291
Worsted crepe	35	220	20	7	1.868	317
Worsted crepe	35	223	20	7	1.901	321

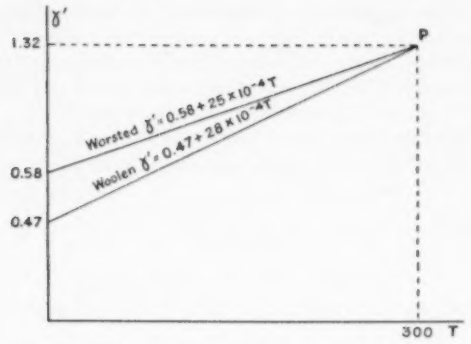

FIG. 8. *Relationship of yarn density and twist coefficient of worsted and woolen yarns extended to point of critical diameter and twist limit.*

It is plain that break will be brought about by the increase in tension undergone by the thread on trying to contract under the twisting action. Point P is not always reached, and break occurs in some cases at lower twist coefficients than expected.

Case B:

Yarns of normal twist were allowed to contract under the twisting action until the contraction reached 25%. The length was then fixed and no further contraction was allowed. Twist was inserted until break occurred. The following results were obtained:

Yarn	N	Initial twist per mm.	Initial tension (g.)	Maximum C (%)	Twist per mm. at break	T at break
Worsted	30	0.605	25	25	1.932	353
Worsted	40	0.671	20	25	2.161	342
Worsted	50	0.622	15	25	2.373	337
Woolen	16.8	0.363	25	25	1.360	332

In this case break takes place at twist coefficients that are always higher than indicated by point P.

Case C:

Twist in the yarn was increased and the yarn was allowed to contract freely. Lengths of 10 cm. were tested and the values for the twist coefficients at break were much higher than indicated by point P.

It should be borne in mind that whenever the freely contracting yarn has reached the highest compactness there appears a characteristic curling of the thread due to the deformation produced by torsion; then the slightest increase in load is sufficient to cause the yarn to break. Such a phenomenon has been revealed through microscopic examination.

The twist limit, theoretically, would coincide with point P and would be the point of critical diameter and the point of yarn breakage. However, the twist limit is not absolute but depends upon experimental conditions. If such a point is considered to be a limit, it is because of its likeness to the concept of critical diameter. Under conditions of twisting which occur in practice, point P will never be reached, since the yarn will break at lower twist values, owing to the effects of loading, radial compression, and torsion. In the twisting of a yarn a contraction of 10% is seldom exceeded.

Table III gives a comparison of values of twist coefficients and diameter coefficients which were discussed earlier.

From equations (12), (13), (14), and (15) the initial yarn densities shown below are found and can be used to calculate the values of tan θ in equation (9) for different yarns.

Fiber	Initial yarn density (γ')
Cotton	0.56 (Besset)
Worsted	0.58
Woolen	0.47
Rayon	0.60

From the above figures it may be seen that the more perfect the yarn the higher the initial yarn density; the figure for rayon is the highest because the yarn is formed of continuous filaments. Worsted yarn, formed of long, fine fibers, is next, followed by cotton, which has shorter fibers, and then by woolen yarn, which has irregular fibers.

We have experimentally studied the variation of contraction in connection with the coefficient of

TABLE III. COMPARISON OF TWIST COEFFICIENT AND COEFFICIENT OF DIAMETER

Yarn	Twist coeff. (T)	Coeff. of diameter (K)
Worsted	95	0.0052
Worsted	110	0.0045
Worsted	220	0.0024
Worsted with dressing	110	0.0027
Woolen	100	0.0050
Woolen	135	0.0048
Woolen with dressing	135	0.0047

twist of wool and rayon yarns. The data show that the results obtained by Besset for cotton can also be used for other fibers, using the above densities and taking into account the fact that the diameter of the average spiral is variable according to the fiber used.

Referring again to equations (9) and (11), we set coefficient E equal to $\tan^2\theta/T_1^2$. To calculate the value of E for cotton we use the following relationship:

$$E = \frac{\pi}{100\gamma'} = \frac{\pi}{100 \times 0.56} = 0.05.$$

To find E for the other yarns, we substituted the experiment contraction values and twist coefficients into equation (11), which has been stated in terms of E:

$$C = 100\left(1 - \frac{1}{\sqrt{1 + ET_1^2}}\right); \qquad (16)$$

and, solving for E, the following results were obtained:

Fiber	E
Cotton	0.05 (Besset)
Worsted	0.06
Woolen	0.04
Rayon	0.11

TABLE IV. EXPERIMENTAL VALUES OF CONTRACTION AND TWIST COEFFICIENT

		Contraction				
	Exp.	3%	8%	13%	18%	22%
Yarn	Anal.	3%	8%	13%	17%	21%
		Twist coefficient				
Worsted 30s		110	186	237	271	305
Worsted 40s		112	184	233	270	312
Worsted 50s		108	180	230	275	308
Average T		110	183	233	272	308
		Contraction				
	Exp.	2%	7%	10%		
Yarn	Anal.	2%	7%	10%		
		Twist coefficient				
Woolen 16.8s		80	178	233		
Woolen 10.5s		120	193	227		
Average T		110	185	230		
		Contraction				
	Exp.	—	5%	11%	19%	
Yarn	Anal.	—	4%	10%	20%	
		Twist coefficient				
Rayon 100 den.		10	73	153	230	
Rayon 150 den.		10	77	145	235	
Rayon 200 den.		10	75	150	225	
Average T		10	75	149	230	

The application of coefficient E is shown in Table IV, and in Figure 9 some of the results are plotted. When the above values are substituted in equation (16), the calculated contractions are in almost exact agreement with the experimental data. Therefore, the contraction caused by twist and referred to coefficient T (turns per meter/$\sqrt{N}$) can be expressed as follows:

Cotton

$$C = 100\left(1 - \frac{1}{\sqrt{1 + 0.05 \times 10^{-4}T^2}}\right). \qquad (17)$$

Worsted

$$C = 100\left(1 - \frac{1}{\sqrt{1 + 0.06 \times 10^{-4}T^2}}\right). \qquad (18)$$

Woolen

$$C = 100\left(1 - \frac{1}{\sqrt{1 + 0.04 \times 10^{-4}T^2}}\right). \qquad (19)$$

Rayon

$$C = 100\left(1 - \frac{1}{\sqrt{1 + 0.11 \times 10^{-4}T^2}}\right). \qquad (20)$$

It must be pointed out that for rayon and other yarns of continuous filament the size and number of filaments can produce some variation in the density and consequently in the diameter.

From E we can obtain the relationship between the diameter of the average spiral and the yarn diameter.

$$d_t = wd,$$

where w is a constant, given as 0.5 for cotton by Besset. Also:

$$\tan\theta = \pi d_t T, \quad d = \frac{\delta}{\sqrt{N}}, \quad \text{and} \quad T_1 = \frac{t}{\sqrt{N}},$$

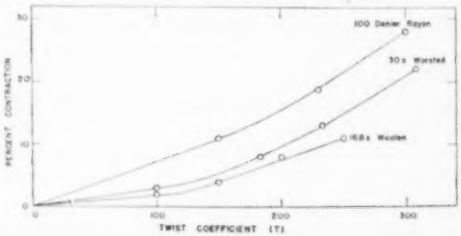

FIG. 9. *Experimental values of % contraction vs. twist coefficient.*

where δ is the diameter coefficient. Thus,

$$\tan^2 \theta = \pi^2 w^2 \delta^2 T_1^2;$$

also:

$$\tan^2 \theta = E T_1^2.$$

Then

$$E = \pi^2 w^2 \delta^2,$$

from which

$$w = \sqrt{\frac{E}{\pi^2 \delta^2}}. \qquad (21)$$

Using $\delta = \frac{2}{10}\sqrt{\frac{1}{\pi\gamma}}$, the values for w were found to be as follows:

Fiber	w
Cotton	0.50 (Besset)
Worsted	0.53
Woolen	0.39
Rayon	0.73 (López-Amo gives 0.66)

There is an explanation for the order of values for w. In the yarns made of continuous filament, the geometrical rules for spiral structure are more exactly complied with and the spirals are therefore more nearly perfect. Hence the average diameters of the spirals are higher than those in yarns of discontinuous fibers. Even in these the values for the average spiral will be different according to the fiber length, for in long fibers the structure of the spirals will be more nearly geometrical than in short fibers; therefore the diameter of the average spiral will be lower for yarns of shorter fibers.

Let us see now the connection between the coefficient of twist and the yarn diameter, considering the contraction influencing the count. Substituting the equation for density (equation (8)) in the equation for diameter (equation (3)), we get the relationship between diameter and twist coefficient (for the inverse metric count N):

$$d = 2\sqrt{\frac{1}{N\pi(a + bT)}}. \qquad (22)$$

But if the yarn is under twist it will also have contraction, which will modify the inverse metric count in the following way:

$$C = \frac{n - n_f}{n}(100),$$

where n is the original N and n_f is the final N. C is also given by equation (16).

Thus the diameter equation corrected for contraction becomes:

$$d = 2\sqrt{\frac{\sqrt{1 + E \times 10^{-4} T^2}}{N\pi(a + bT)}}. \qquad (23)$$

The results obtained by use of this equation are presented in Table V and Figure 10 for worsted, woolen, and rayon yarns. The analytical diameters were all calculated in this manner. The experimental and calculated data compare very closely.

Finally, concerning plied yarns, for the contraction caused by twisting we can employ Besset's equation, taking the value E corresponding to the yarn fibers.

Calling T_1 and T_2 the coefficients of twist for each yarn and T the coefficient of doubling, the Besset

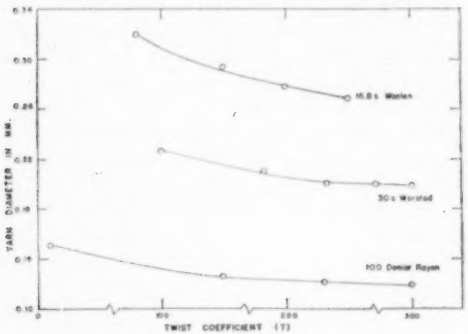

FIG. 10. *Experimental relationship between yarn diameters and twist coefficients.*

TABLE V. COMPARISON OF CONTRACTION AND DIAMETER VALUES

Yarn	Coeff. of twist	% contraction Anal.	% contraction Exp.	Diameter in mm. Anal.	Diameter in mm. Exp.
Worsted 30s	100	3	3	0.228	0.227
	183	8	8	0.211	0.211
	233	13	13	0.205	0.205
	272	17	18	0.200	0.203
	308	21	22	0.197	0.199
Woolen 16.8s	100	2	2	0.320	0.320
	150	4	4	0.296	0.294
	200	7	8	0.280	0.278
	250	11	11	0.268	0.269
Rayon 100 den.	10	—	—	0.151	0.151
	149	10	11	0.127	0.126
	230	20	19	0.120	0.121
	300	29	28	0.119	0.119

formula gives the following expression for percent contraction:

$$C = 100\left(\frac{1}{\sqrt{1 + ET_1^2}} - \frac{1}{\sqrt{1 + ET_2^2}}\right) - \left(1 - \frac{1}{\sqrt{1 + ET^2}}\right). \quad (24)$$

It must be noted that a positive value within the parentheses represents a lengthening and a negative value represents a contraction. According to the direction of twist of each yarn and the direction of the ply twist, either a lengthening or a shortening may occur.

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INDUSTRIAL SECTION

High-Speed Motion Pictures in Textile Research

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Abstract

Motion pictures which depict action greatly slowed down are of unique assistance in analyzing complex machinery and processing operations. In recent years cameras for taking high-speed motion pictures have become generally available, and the technique for their use is easily acquired. Although their application in the textile industry has thus far not been extensive, it is probable that textile engineering and production departments will find high-speed motion pictures a valuable aid in analyzing defective machinery, in "trouble-shooting," and in the development of new processing methods. This article includes a description of the types of cameras used, special details on technique, a comparison with other methods for viewing action, and illustrations of some of the applications.

Introduction

The high-speed motion-picture camera has been called a "time microscope" because it enlarges the time scale by several hundred times. Action which is too rapid to be perceived by the eye is slowed down so that details may be studied at leisure. Like the microscope, the high-speed motion-picture camera brings an entirely new perspective to commonplace things. The technique of high-speed motion pictures is employed in studies as diverse as the analysis of machine motion (cams, gears, clutches), flame propagation, locomotion of the sea horse, cavitation following the entrance of rapidly moving objects into water (torpedoes), and surface-tension measurements by means of vibrating drops. In the textile industry, studies on loom motions, drafting, and spinning have been made, but only a few reports have been published, and in the past the films have not been generally available. The results were intended primarily as an aid to improved engineering design. In general, applications of high-speed motion pictures in textile processing and research appear to be relatively few in number, but the cameras now available are eminently practical, and it is to be expected that wider use will be made of them. The films are, moreover, of great value in teaching, and are unsurpassed in aiding the exposition of the complicated and rapid motion of machinery.

This article is a résumé of recent experiments in the application of the camera to textile problems. The initial objective was to determine the capabilities of the instrument, and for this purpose a variety of subjects were chosen, including the following: (1) card, drawing and spinning frame, and loom operation; (2) yarn and cord breaks; and (3) wetting phenomena.* Examples of some of the motion pictures taken are reproduced in the form of enlargements of single frames from the motion-picture film. Because the technique is relatively new and because high-speed motion pictures are frequently confused with visual observation by means

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* This article is concerned primarily with the use of the high-speed motion-picture camera in textile processing. Several other applications, including the measurement of surface tension by the oscillating-drop method and the water-repellency of treated fabrics, will be covered in separate papers. In this connection the reader is referred to an analysis of waterdrop impact by means of the Zeiss camera reported by Kärrholm and Kärrholm in this issue, page 215.

of stroboscopic illumination and with still pictures taken with microflash equipment, a brief preliminary discussion and comparison of these other techniques is included. (See Table I.)

TABLE I. COMPARISON OF METHODS FOR VIEWING RAPID MOTION

System	Advantages	Limitations
Stroboscope viewing	Simplicity Convenience	Useful only on repetitive motion Image formed by successive positions of moving object Visual observation; no record
Microflash still photography	Large negative	Pictures taken of moving object at successive positions in different cycles
High-speed motion pictures	Actual, complete sequence of action Useful for non-repetitive action	Small image size

Methods for Viewing Rapid Motion

Visual Observation

Objects which perform repetitive motion (*e.g.*, the traveler on a spinning frame) can be viewed directly with a shutter which interrupts the view in synchronization with the motion; this method is used when the object is reflecting light. The moving object can be made to appear as if it were standing still. A similar result is obtained by light flashes from a stroboscope unit in synchronization with the action [6, 14]; this method is usable only when the general illumination of the object in action is of low intensity. The result is that the action appears to cease or to proceed at a low speed. It must be realized, however, that a complete sequence of action is not viewed by this method, since successive positions of the moving object are observed. This is an important characteristic of the method of stroboscopic viewing.

Still-Camera Photographs

Cameras with focal plane shutters are capable of exposures up to 1/1,500 sec. For some purposes, satisfactory photographs of motion can be obtained, but serious distortion of the image is always present. Other shutters of the type designated as "between-the-lens shutters" have a top limit of 1/500 sec. and are of limited utility. The speed limitations of mechanical shutters are overcome by means of light flashes of extremely short duration, which is often referred to as the "microflash" method [4, 6]. The exposure range is from 1/5,000 to 1/1,000,000 sec. Various devices employed to synchronize the flash with the action are available. With this technique, a single picture is obtained which has the advantage of a large plate size (*e.g.*, 4 in. × 5 in.) suitable for considerable enlargement and study of fine detail. A series of such photographs taken at different positions of the moving object may then be assembled to form a picture sequence. As in stroboscopic viewing, however, a complete record of a single cycle is not obtainable, and the sequence of pictures represents the repetitive action at different cycles. This technique has been used to advantage by Sepavich and Palmer [16] in the photography of shuttle motion; Hawkins and Balleisen [7] describe other applications. The microflash technique is sometimes varied by keeping the shutter open during a series of flashes which follow each other at very short intervals; a multiple image is obtained which shows the position of the moving object during an entire sequence. Pictures of this kind have proved of popular interest, and those of such subjects as the swing of a golf club, the antics of ballet performers, etc., are frequently reproduced in various publications.

Motion-Picture Cameras

Motion-picture cameras, in which the film travels at a high speed through the camera, have been developed in the last 10 years to an eminently practical state. Pictures taken at a high speed and projected at the normal speed show a slowing down of the motion. The designation "high-speed motion-picture camera" indicates the rate at which the film moves in the camera; the result, on projection, is "slow-motion" or "ultraslow-motion" pictures. Sound pictures are taken and projected at the rate of 24 frames per sec. (f.p.s.); silent pictures are taken and projected at 16 f.p.s. The action then appears to be normal, for there is no change in the time scale or time axis. The usual "slow-motion" pictures are taken at speeds around 128 f.p.s., and some cameras have been made which operate at speeds as high as 256 f.p.s. These cameras depend upon intermittent film movement: the film is positioned at the gate of

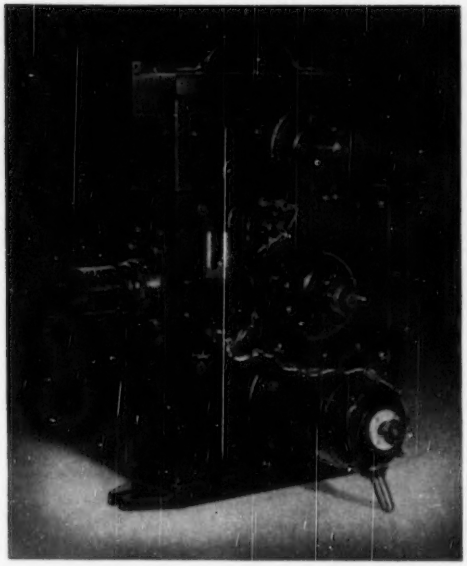

Fig. 1. *Edgerton High-Speed Motion-Picture Camera.*

the camera, a mechanical shutter opens and exposes the film, and then blocks out the light; the film is advanced to the next frame, and the sequence is repeated. Because of mechanical limitations, it is not feasible to increase the taking speed much beyond 256 f.p.s. with an intermittent film movement.

Higher film speeds in the camera are obtained by a continuous film movement which avoids the strains on both the mechanism and the film produced by an intermittent motion. Separate pictures are obtained by (1) a spark discharge synchronized with the film movement, (2) a rotating optical shutter, or (3) a combination of the two. Cameras of these types are in use. The Edgerton camera, which is of the first type, has proved to be very versatile [6]. (See Figure 1.) The flash provides a very short exposure and the image, in consequence, is very sharp.

A camera using the rotating optical shutter has some advantages. The camera itself is self-contained and is of moderate weight (30–50 lb.), and hence it is portable. Lighting from a continuous source which is independent of the camera, and not synchronized, may be adapted to the subject. Thus, self-luminous subjects can be photographed; these include, for example, furnace operations, lamp burn-

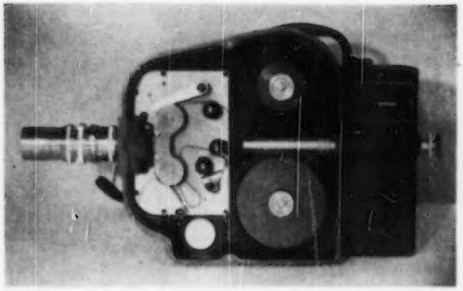

Fig. 2. *Eastman Type III High-Speed Motion-Picture Camera, showing film transport mechanism.*

outs, etc. The Eastman (Figures 2 and 3) and Fastax 16-mm. cameras are of this type.

The method for image formation in the Eastman camera is shown in Figure 4. The light from the subject passes through the lens and is prevented from reaching the film by the opaque end of the prism (Figure 4A) until the film has advanced to the position for exposure. As the optical shutter rotates, the light passes through the plate to the film and, because of the angle of the optical plate to the film, the light ray is refracted upward (Figure 4B). The degree of displacement decreases until the plate reaches a vertical position where the path

Fig. 3. *Eastman Type III High-Speed Motion-Picture Camera, showing starting rheostat control.*

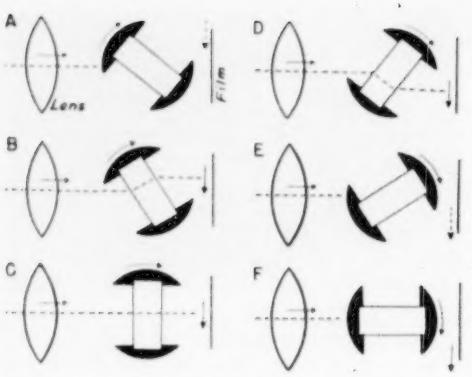

FIG. 4. *Diagram of optical plate with shutters used in Eastman Type III Camera.*

of the light is straight through the plate (Figure 4C). Continued rotation of the plate causes the light ray to be deflected downward (Figure 4D) until it is blocked off by the opaque end of the prism (Figure 4E). In this way the image travels with the film during exposure [2]. The Fastax camera uses a different prism, but the principle is identical. The exposures for the prism cameras are in the range of from 1/15,000 to 1/50,000 sec. at the maximum film speeds.

The cameras described above are commercial instruments. They can be used successfully by any person skilled in photographic technique.

Numerous other cameras have been constructed, but many of these are experimental models which have been developed for special purposes. One of the first cameras was designed by C. F. Jenkins in 1910. This camera operated at a maximum speed of 3,000 f.p.s., and the images were formed by a series of matched lenses on a rotor which turned in synchronization with the film. This principle has been used in other cameras; one variant is a set of mirrors. A feature common to some designs is a large drum on which a length of film is wound. The drum is rotated at high speed and at the proper moment the accessory equipment is actuated and a sequence of pictures is recorded. With this design, very high speeds are possible: recently a camera capable of taking 10,000,000 pictures per sec. has been described. At these very high speeds, images are obtained which are arranged in sequence by means of an "image dissector" and assembled by process printing to form a motion picture suitable for projection. Such instruments are used in studying ballistic and shock-wave phenomena; but they are not properly classified as motion-picture cameras.

For most industrial purposes, film speeds of less than 10,000 f.p.s. are ample, and the results, as motion pictures, are highly satisfactory. Sandell [15] in reporting on the definitions adopted by the Committee on High-Speed Photography of the Society of Motion Picture Engineers gives the following classifications: *High-speed photographs*—"still" pictures taken at shutter speeds of less than 0.001 sec.; *High-speed motion pictures*—pictures taken at a rate between 250 and 10,000 f.p.s.; and *Ultrahigh-speed photographs*—pictures taken on "strip cameras" at speeds in excess of 10,000 frames per sec.

Some idea of the degree to which motion is slowed down by means of high-speed motion-picture cameras can be obtained from the following comparisons. A roll of 100 ft. of film exposed and then projected at the normal speed of 16 f.p.s. takes about 4 min. At 3,000 f.p.s. photographing speed, the 100-ft. roll of film is exposed in 1⅓ sec. and the viewing time is again 4 min., resulting in a visual deceleration of motion of approximately 200 times.

Practical cameras for field use must, of course, be portable and suitable for location shots. Further, the cost of operation, particularly for film and maintenance, should be reasonable. The three cameras made in the United States and described above meet these requirements. (See Table II.)

It can be expected that the high-speed camera will find an important place in textile research in the future. One study on loom motion by means of slow-motion pictures is by Palmer and Ramsdell [13]. Motion pictures taken at 188 f.p.s. were used, and the pictures were analyzed by projection as stills. Other studies of this type are known to

TABLE II. HIGH-SPEED MOTION-PICTURE CAMERAS MADE IN U.S.A.

Camera	Image-forming mechanism	Maximum speed (f.p.s.)	Film size (mm.)
Eastman Type III	Prism	3,000	16
Fastax 16	Prism	5,000	16
Fastax 8	Prism	10,000	8
Fastax Wide angle	Prism	3,500	35
Edgerton (General Radio)	Synchro flash	1,500	35

have been made, however, and the results have been used in altering machine design, but the results have not been published. A training film which includes high-speed motion pictures has been announced recently [12].

For those who may wish to investigate the subject further, a bibliography of pertinent references is included. The list prepared by the Eastman Kodak Company [3] includes citations to many articles on special applications, such as ballistics, combustion, electrical phenomena, etc. In general, the literature is scattered, and an adequate compendium of information is not available. The book by Tupholme [18], however, has a helpful section on the subject, and numerous illustrations of the several techniques are given by Edgerton and Killian [5]. Recent review articles describing equipment and technique are useful [7, 8, 10, 14, 17, 19], and manufacturers' brochures provide detailed descriptions of available equipment [2, 6, 20]. The Society of Motion Picture Engineers is now holding symposiums on high-speed photographs at their semi-annual meetings. The proceedings of the first symposium, held in 1948, have been published as a supplement to the March, 1949, issue of the *Journal of the Society of Motion Picture Engineers*, and the papers given at the second symposium appeared in the November, 1949, issue of the same journal.

Technique

The technique for taking high-speed pictures is quite different from that for conventional motion pictures, although expertness with a standard-speed, precision motion-picture camera is a great asset to the high-speed photographer. Important differences are the following. Each scene requires one 100-ft. roll of film. At the highest camera speeds, the camera is accelerating during the first 40 ft. of film; the most useful part of the film is the last 60 ft. The whole scene is filmed in a matter of a few sec., and close coordination is required to be certain that the action occurs in the short interval that the camera is running. Since the exposure cannot be reliably estimated with meters, a trial roll is exposed and developed as a negative for each scene which presents new photographic conditions; the density of the negative offers a guide for the adjustment of lighting and lens aperture. The negative film is useful also for enlargements of a sequence of single pictures. Reversal film, processed by the manufacturer, is used for the positive prints intended for projection.

Some of the important details for filming are noted below, but the following general conditions apply to the filming of many subjects: *Illumination*—6 to 8 General Electric Photospot lamps, internal reflector type, RSP-2, 500-watt, placed 18 to 36 in. from the subject and as close to the camera axis as possible. *Film*—Eastman 16-mm. Super XX (Weston rating 80, tungsten). *Lens aperture*—f 4 to f 8.0, depending upon color of subject and distance of lamps from subject, at speeds from 1,000 to 3,000 f.p.s.

The illumination must be intense. Various studio lamps are available, but these units are heavy and cumbersome and cannot be used successfully in crowded quarters. Our results with the 500-watt Photospot lamps have been generally satisfactory, but care must be taken to avoid damaging the lamps during transit and while preparing the scene, for several lamps have exploded. A new lamp, announced recently, is the General Electric 750R photographic lamp. It is designed to operate at about

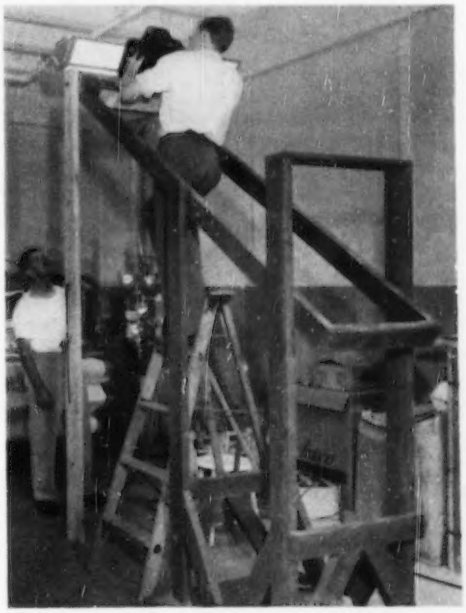

Fig. 5. *Scaffold used as camera support for high elevations.*

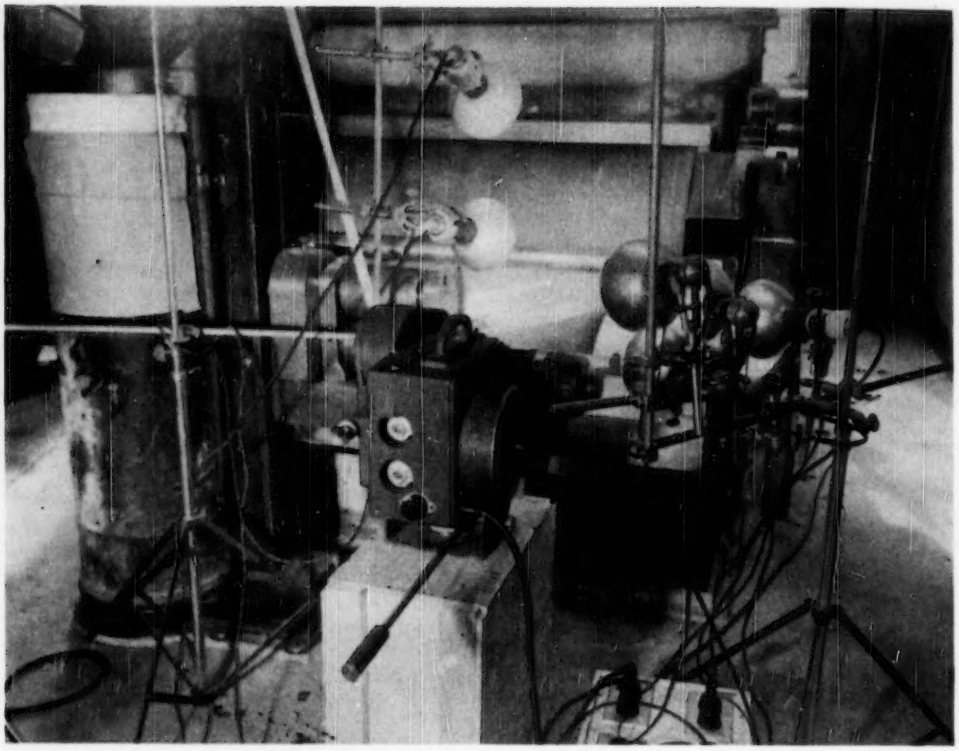

FIG. 6. *Arrangement for photographing card web and doffer.*

18 in. from the subject. The lamps are held with laboratory clamps on a metal framework of 0.5-in. aluminum rods. This arrangement is advantageous because the assembly is compact and portable and a maximum range of adjustments is possible. For convenience in arranging and focusing the camera, and in order to provide preliminary illumination without heating the subject excessively, the lamps are connected through a series-parallel switch box; when the set-up is being prepared the lamps are in series, burning dimly, and just before filming the scene they are switched to parallel connection and full brightness.

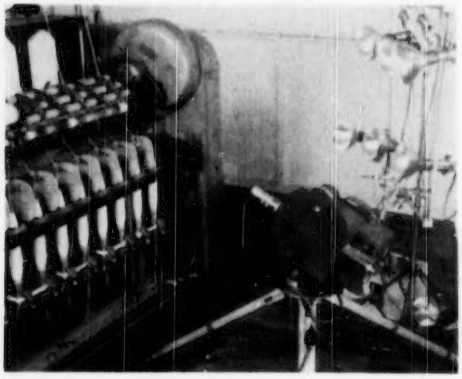

FIG. 7. *Arrangement for photographing spinning frame.*

A heavy tripod and tilting top serve adequately as a camera support for many subjects. For photographing machinery from higher elevations (to heights of about 12 ft.) and vertically downward, an adjustable scaffold was constructed. (See Figures 5, 6, 7.) Some cameramen have constructed a camera support from a drill-press stand; this unit is especially useful in close-in work.

For timing action the newer cameras have built-in glow lamps which produce 120 "pips" or marks per sec. when operated on 60-cycle A.C. current, thus giving a measuring unit of 8⅓ milliseconds. An oscillator is now available which provides 1,000 "pips" per sec. [1]. We have found synchronous motors which turn at 1,800 and 3,600 r.p.m. to be quite satisfactory. A dial, 1 in. in diameter, is attached to the motor shaft and is marked with a pointer. The motors are mounted on small brackets which can be clamped or held by hand during filming in the field. The observation of elapsed time is measured on successive single frames of the film by measuring the rotation with a circular protractor. The time interval can be readily computed. (See Figure 11.)

Because of the short exposure, fast films are necessary. Eastman 16-mm. Super XX (available in negative and reversal types) are the most commonly used, but the Eastman Linagraph films are also spooled for high-speed cameras, and they have the advantage of about twice the speed of the Super XX films but the disadvantage of somewhat greater graininess. As noted previously, a trial film is exposed and developed for each scene which presents different photographic conditions. Development of the negative Super XX film is accomplished in a Morse film tank using Eastman D-19 developer for 14 min. at 20°C. The negative film can, of course, be projected, and suitable compensation may be made for lighting, depth of field, film speed, etc., before proceeding with the filming. The negative film is useful also in making single-frame enlargements of a sequence of frames. A size suitable for record purposes is 5 in. × 7 in., but enlargements have been made to fit the standard 11 in. × 14 in. salon mount. At the latter size the graininess of the film is quite noticeable.

The final pictures can be studied by projection in a standard motion-picture projector, by means of an "action" viewer which allows more leisurely examination of the important scenes, or by a sequence of prints.

Certain special problems arise in high-speed motion-picture photography which cannot be precisely defined or evaluated. One of these can best be described as "the art of the medium," for it calls for judgment and understanding apart from the more mechanical attributes of technique. A partial analysis can perhaps be made in terms of resolution, image quality, the balance of field size and rate of movement, and, finally, the skill and knowledge of the persons seeking to evaluate the films. To some extent these are problems common to any pictorial representation, but in high-speed motion pictures they are determined by the specific requirements of a film suitable for detailed analysis.

The appearance of sharpness of image in the projected film is a composite of optical and psychological factors. The resolving power of the lens-camera-film system, however, establishes the image quality. The lenses used have a resolving power of 60–80 lines per mm. at f 5.6, and the Super XX reversal film is said to resolve 70 lines per mm. [9]. It is our impression, gained from tests with the same lenses in a conventional motion-picture camera (Cine-Kodak Special) and from measurements on the exposed films, that the resolving power of the film is the more important factor, despite the apparent equivalence of the lenses and film in potential resolution. The requirement of maximum resolution becomes critical when the motion of single fibers is to be observed in a field of sufficient width to display the action effectively; it is also critical when measurements are being made on the processed film by means of an optical micrometer.

Since the motion to be photographed is continuous, there is a corresponding movement of the image on the film which contributes to a seeming impairment of resolution or, as viewed, to blurring. With more rapid exposures, less traveling of the image results, and the cameras which depend upon a microflash lighting system provide generally better image quality. For the rotating-prism camera, the following empirical formula has been given as a guide to the selection of field width and film speed for satisfactory images [2]:

$$F = 40 \times S/W,$$

where F is the picture frequency in f.p.s., S is the speed of the subject in in. per sec., and W is the field width in in. This method of estimation is shown graphically in Figure 8. In many cases, however, the speed of the moving subject is unknown and the purpose of the photography is to determine this speed. In certain other cases, very complex motion (such as frequency of vibration) is to be analyzed, and no estimate of the speeds can be made; this procedure is, accordingly, of limited usefulness.

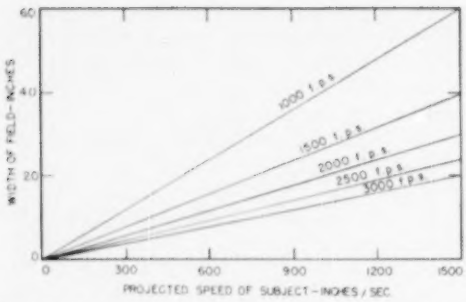

FIG. 8. *Curve for selection of photographing conditions (camera speed, field width) for known object speeds.*

There are, in addition, certain imponderable psychological factors connected with the rating of image quality which cannot be stated explicitly. During the viewing of motion pictures, a slight amount of blurring is not objectionable and may actually improve the appearance of motion. Moreover, graininess of the film, which is objectionable in single-frame enlargements and in the study of the films under low-power microscopy, becomes much less apparent during projection, since the grain pattern from one frame overlaps that of succeeding frames.

More important is the selection of photographic conditions providing the necessary delineation of motion and form, together with adequate resolution, for these provide the basis for understanding the action photographed. In many scenes it is desirable to resolve single fibers and at the same time to include a sufficiently large field to show the entire action adequately. An example of such subjects is the heddle action on a loom, where the tangling of loose fibers on the warp yarns produces a surge in the passage of the yarns past each other. The resolving power of the lenses and fast film is adequate for this requirement if the field width is not greatly in excess of 12 in.

In taking pictures of machinery operation, it is essential that some control of the action be obtained. At the highest camera speeds there is from 0.5 sec. to 1 sec. for filming the action. A yarn break, for example, must be predictable to within about 0.5 sec., and for this reason it is not practical to set up a camera and photograph a spinning frame until a break takes place. The break must be caused by the operator at the proper time in order to synchronize with the camera. In cases in which the action can be initiated by an electrical circuit, the electrical signal can be given by a mechanism within the camera. Successful filming of such action requires that the operator select experimental conditions which simulate those of the actual event as closely as possible.

There is, finally, one aspect which needs emphasis. The person who has had experience with the action to be photographed and who has given thought to its mechanism is the one best fitted to assist the photographer in the selection of camera position, taking speed, lighting, and other photographic conditions. He is also the person who by training and understanding can observe more in the films than one who is unfamiliar with the process. Successful use of the medium thus requires collaboration of professional and production personnel. It has happened that the motion pictures merely provided vis-

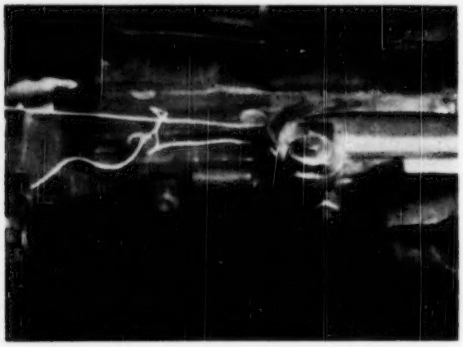

FIG. 9. *Fill yarn loop on return of shuttle.*

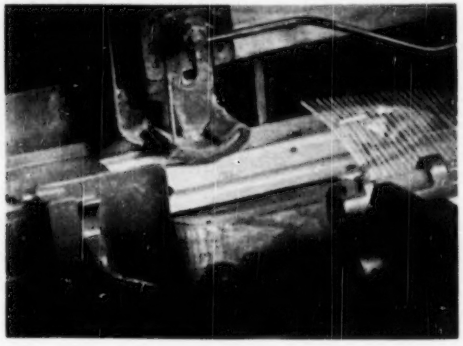

FIG. 10. *Shuttle entering shed.*

ual confirmation of action which had been inferred from theory, but the pictures are most useful, of course, where the precise nature of the action is unknown or where some part, as in a machine, is not functioning properly.

Examples of Applications

The full effectiveness of high-speed motion pictures can be judged only by projection; enlargements of single frames do not adequately convey the dynamic nature of the subject. Illustrations taken from enlargements will, however, indicate some of the applications with which the authors have had experience.

Scenes taken from a group of loom pictures are reproduced in Figures 9 and 10. As the shuttle starts on its path, the trailing fill yarn forms differently shaped loops with each pick. With lively yarns, twisting and looping occur which are not always removed as the slack is taken up by the advancing shuttle. In several production looms photographed, the shuttle has been observed to be in contact with the warp yarns for the entire width. As the shuttle entered or emerged from the shed, the warp yarns were observed to be riding on the edge of the shuttle. A similar scene has been reproduced in the article by Jones and Eyles [8]. Contact of the shuttle with the warp yarns near the center of the warp was

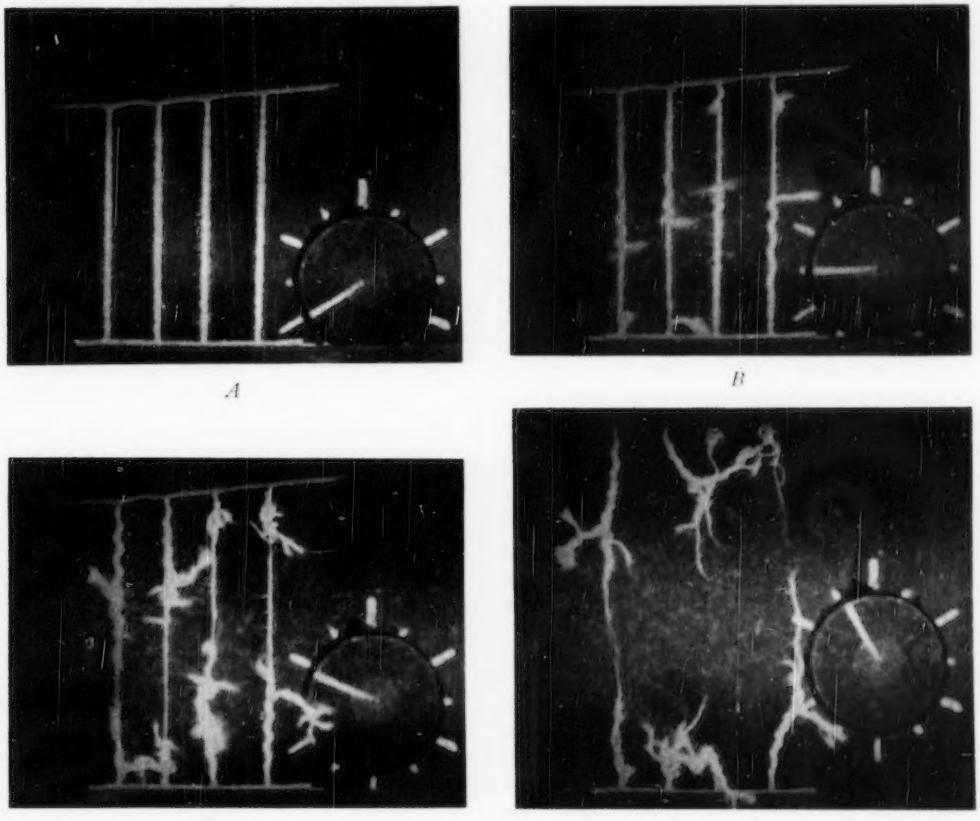

Fig. 11. *Cotton tire-cord breaks. (In scene A, cord is shown considerably stretched; in scene B, some plies have broken; in scene C, most of the plies have broken; and in scene D, the break is complete and the field is filled with fiber fragments. Time lapse between scenes is 1/360 sec.)*

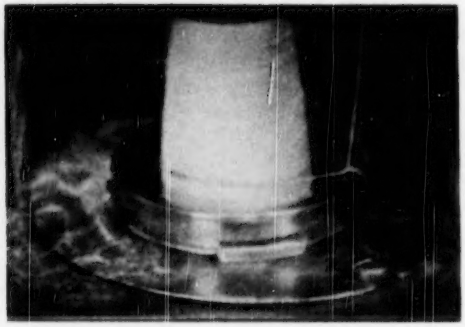

FIG. 12. *Traveler on spinning frame.*

photographed by dyeing the warp black and photographing directly down on the warp. When the shuttle is completely clear of the shed, the warp yarns are noticeably slack.

In a study of heddle action on an experimental loom, it was observed that the loose fibers on adjacent sized cotton yarns tangled as the harness changed position. The drag on the yarns was appreciable, and the entanglement was broken suddenly as the heddle pulled the yarns into position. These scenes, considered with the observations of the travel of a shuttle through the warp, clearly indicate that an effective warp size should increase the resistance to abrasion and smooth the yarn surface by causing the fibers to adhere in alignment with the long axis of the yarn.

Yarn and cord breaks are of great importance in textile processing, and visualization of the mechanism of breakage can be of assistance to the operator. A laboratory instrument was devised to break yarns and cords under controlled conditions. It consisted of a fixed lower bar and a pivoted upper bar; the yarns were stretched under light tension between the two bars, taking care not to lose twist in the fastening operation. The yarns were broken at the proper moment when the camera was running by means of rapidly raising the upper bar. Unsized cotton 16s yarns were observed merely to pull apart, with the fibers slipping past each other. Sized yarns, on the other hand, break sharply as if each yarn were a rod, with the individual fibers securely bound by the sizing material into a bundle. The time for the actual break of sized yarns is a small fraction of a second. The illustrations in Figure 11 show a typical 3-ply tire-cord break. In the case of cords, the break also occurs in a short time interval, but it is preceded by a period of stretching (about 0.2 sec.), with the break occurring sharply (about 0.002 sec.). When the cord breaks, the field of view is quickly filled with fragments of the fibers which formed the plies; when breakage occurs, fibers are sheared into short lengths.

Yarn breaks occurring during spinning of cotton yarn were successfully filmed. Breaks caused by a thin spot in the roving occur usually at the exit of the rolls, and the time interval for the break is extremely short. Such a break is caused by the fibers pulling away from each other, and the camera does not reveal much detail. When the break is caused by a slub, however, the course of the yarn may be followed for more than a second, until the actual break occurs, again in a hundredth of a second or less. In one scene, a slub was followed from the rolls through the pigtail to the balloon where the break actually took place.

The traveler on a spinning frame is shown in Figure 12. This subject is important and worthy of an extended study, but in order to photograph it satisfactorily camera speeds estimated as greater than 5,000 f.p.s. are necessary. The illustration shows a traveler running at 9,200 r.p.m., photographed at 3,000 f.p.s. For greater detail, a closer position of the camera and higher camera speeds are required.

Acknowledgment

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A Simple Quantitative Test for the Felting of Wool Top*

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Abstract

A simple, rapid procedure for evaluating the feltability of wool in the form of top is presented. The method consists of subjecting a sliver to controlled wet mechanical action, and measuring its change in length. It yields results which correlate well with the shrinkage during laundering of garments made from the top; the method thus provides a useful tool for controlling the application of some chemical shrink-resistant treatments in the mill. In addition, this method shows promise of usefulness as a tool for investigating the nature of felting.

THE GROWTH of interest in shrink-resistant wool during the past decade has been evidenced by an increasing volume of literature in the field and by the entrance into commerce of a variety of processes for the production of felt-resistant yarns and fabrics.

Evaluation of the effectiveness of a process has usually been made in terms of the behavior during laundering of a garment or fabric; when wool is treated in the top form, a considerable length of time must elapse in the course of normal mill practice before material is available for quantitative evaluation. This time lag is undesirable from the point of view of control, and particularly so in the developmental stages of a new process.

In view of the many unsolved problems in the field, and the current widespread interest in shrink-resistant wool, it was considered desirable to describe a test which was developed for the purpose of measuring the shrink-resistance of wool in the top form, and which has found use in fundamental studies as well. The basic requirements for such a test are as follows: (1) It should distinguish quantitatively between wools which have been treated to impart various degrees of shrink-resistance; (2) It should be rapid and convenient in order to permit its use as a control method in the mill; (3) The results should relate to the shrinkage behavior of garments made from the treated wool.

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The method which was developed, and which fulfills the above requirements, has been used with considerable success in this laboratory and in several mills. It involves the measurement of the change in length of a sample of top after it has been subjected to wet mechanical action. It is the purpose of this paper to describe the method, which is henceforth termed the "top shrinkage test," and to indicate its potential usefulness as a control method and as a tool for fundamental studies.

Description of the Top Shrinkage Test

General Description

The top shrinkage test involves subjecting a sample of top to wet mechanical action under controlled conditions, and measuring its change in length. In order to prevent the sliver from disintegrating or felting to its neighbors, the specimens were sewn into cheesecloth sacks. The stitching at the ends has the additional function of serving as gage marks for measuring the length. The method includes relaxation of the specimens in order to remove strains, followed by tumbling for an appropriate length of time (10 min. in the standard test) in any desired medium. The details of the method of preparation of samples and particulars of the "standard" test used for control purposes in the mill are given below; the bases for the choice of the specified conditions are presented in the Results and Discussion section.

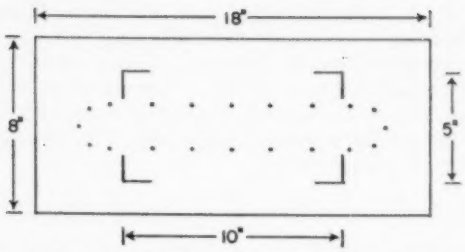

FIG. 1. *Marking of cheesecloth and placing of top in preparation of specimens for top shrinkage test.*

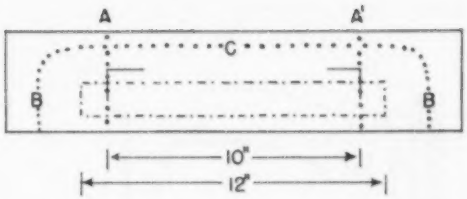

FIG. 2. *Sewing of top into cheesecloth sack.*

Standard Top Shrinkage Test

A piece of cheesecloth or gauze 18 in. × 8 in. is cut, and the four corners of a 10 in. × 5 in. rectangle are marked for reference points, as shown in Figure 1. The type of gauze used is not critical, provided that it is reasonably open in structure; Johnson & Johnson 20 × 12, 18-in. oval bolt has been found satisfactory. A template is convenient for cutting and marking the gauze.

A sample of top is cut 12 in. long, disturbing the structure and fiber alignment as little as possible during the cutting. The sample is placed in the center of the gauze, as shown by the broken lines in Figure 1, and the long edges of the gauze are folded together, enclosing the top so that the marks are superimposed.

The top is secured to the bag, as shown in Figure 2, by rows of stitches sewn at A and A', and enclosed in the bag thus formed by rows of stitches sewn at B and at C. The stitching at A, A' and at C passes through and along the reference marks. The stitching at B and C passes through the gauze only and serves to enclose the free ends of the top sample. In order to avoid erroneous results, care should be taken not to sew the top specimen to the gauze along C. The raw cut ends of the gauze may be folded under and secured when stitching row C.

Four specimens of top which had been treated for shrinkage control and one specimen of the same top untreated are tested simultaneously. Alternatively, or if the same top is not available, another type of top of known shrinkage behavior may be used as the untreated control. The five specimens are immersed in not less than 1 liter of 1% sodium bisulfite solution, squeezed once to aid in wetting-out, and allowed to soak for not less than 10 min. The excess liquid is removed by squeezing once, and the initial length at the center of the top between points A and A' is determined to within the nearest 0.1 in. with a scale. This measurement is made by suspending the wet specimen vertically from a spring clip placed at the top of the test specimen, and clamping the top and gauze bag above but near to the upper reference mark and stitching at A. Another clamp, weighing approximately 300 g., is similarly hung at the bottom of the test specimen just below A'. The initial length, I, is then measured between A and A' while the specimen is thus suspended.

After measurement the specimens are removed and placed in a tumble jar with a fresh 1-liter portion of 1% sodium bisulfite solution at 25 ± 2°C. The jar is approximately 6 in. in diameter and 12 in. high, and is equipped with a leakproof screw cap. The jar is mounted on a set of bearings in the middle and coupled through a speed-reducing drive to a motor so that the jar may be tumbled end-over-end at a constant rate of 60 ± 2 revolutions per min. The tumbling apparatus, which is shown in Figure 3, is identical with that used in the dynamic absorption test for water-repellency [7]. Although the specified jar is hexagonal in shape, this detail is not important to the method; closely similar results are obtained using a cylindrical museum jar of similar dimensions, obtainable from laboratory supply houses.

After tumbling for 10 min., the samples are removed, squeezed once by hand to express the excess liquid, and the specimen length, F, between the reference marks is determined as previously described.

The top shrinkage (%) is calculated from the relationship:

$$\text{Top shrinkage} = \frac{I - F}{I} \times 100,$$

where I is the initial and F is the final dimension. The mean % shrinkage of the treated top is reported to the nearest whole number.

A general idea of the appearance of the sewn specimens can be gained from Figure 4. This shows

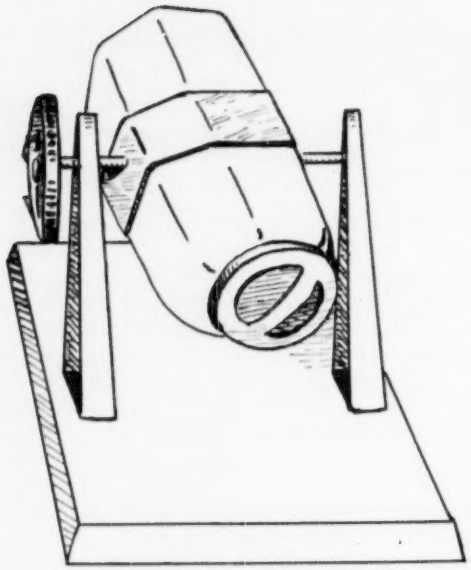

FIG. 3. *Sketch of tumble-jar apparatus.*

a specimen before tumbling, a moderately chlorinated sample after 10 min. of tumbling, and an untreated specimen after 10 min. of tumbling. The marked change in length of the untreated specimen (45%) reflects the felting of the sample, which can readily be observed by opening the sack. In contrast, the fibers in the treated specimen (top shrinkage 10%) are quite free and unfelted.

Reliability of Measurements

In order to estimate the inherent variability of the "standard" top shrinkage test, 16 measurements were made using a chlorinated top which had been thoroughly blended by 28 doublings. The mean value was 15.6%, with a coefficient of variation of 14% and a standard error of the mean of 0.66.

Results and Discussion

Preliminary experiments were performed using soap solutions in the tumble jar and an initial temperature of 50°C in order to simulate the conditions of laundering. Although these experiments yielded reasonably good results, their reproducibility was poor, because variations in the amount and character of the suds affected the severity of the mechanical action. Attention was therefore directed to buffers and other systems which contain no foam-producing materials. The effects of varying some of the experimental conditions are discussed below. In all of these experiments the tests were performed with five specimens constituting a "load," and, unless otherwise specified, the temperature was 25°C and the time of tumbling 10 min.

Effect of Time of Tumbling and Volume of Liquid

Figure 5 shows the top shrinkage of samples of untreated wool which had been tumbled in water for different periods of time, the data being plotted on a logarithmic time scale merely to permit inclusion of a greater number of observations on the same graph. The upper curve in this figure represents results for samples which had been tumbled with 1 liter of water in the jar; the lower curve represents corresponding results when the jar contained 5 liters of water. As might be expected, the rate of felting is quite high initially, whereas after 15 or 20 min. the

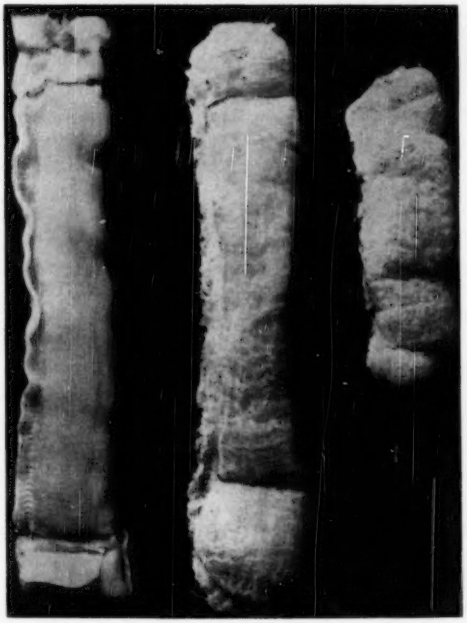

FIG. 4. *Appearance of test specimens for top shrinkage test.* Left—*Specimen before tumbling.* Center—*Sack with shrink-resistant top after 10 min. of tumbling.* Right—*Sack with untreated top after 10 min. of tumbling.*

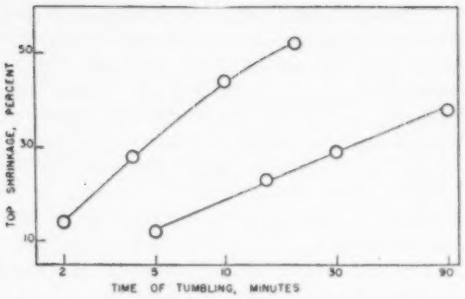

Fig. 5. *Relationship between top shrinkage of untreated wool and duration of tumbling.* Upper curve—*1 l. of liquor.* Lower curve—*5 l. of liquor.*

tightly matted condition of the samples inhibits further change; this is shown by the approximately linear form of the semilogarithmic plots in Figure 5, which is quite typical of results obtained in a wide variety of media. It has been found useful to measure the top shrinkage value at 4 min. (in 1 liter of liquid) in order to characterize the initial rate of felting of a wool; the value at 10 min. has found application in the control tests designed to correlate with shrinkage results after repeated laundering.

The lower curve in Figure 5 demonstrates the large reduction in the intensity of the test which results from increasing the volume of water used. This effect is entirely analogous to that occurring in a wash wheel when low or high water levels are used. Although the possibility has not yet been investigated, it appears likely that increasing the volume of liquid used in the top shrinkage test may prove useful in obtaining close correlation with mild types of laundering, such as washing by hand.

TABLE I. Effect of Temperature on Top Shrinkage Value of Untreated Wool

Reagent	Temperature (°C)	Top shrinkage (1 liter) 4 min. (%)	10 min. (%)	20 min. (%)
Water	25	15	31	40
	40	23	38	47
	50	26	42	49
H_2SO_4 (1% by volume)	25	27	44	53
	40	36	51	59
	50	40	54	60
NaCl (3*M*)	25	13	26	36
	40	21	34	44
	50	22	39	47

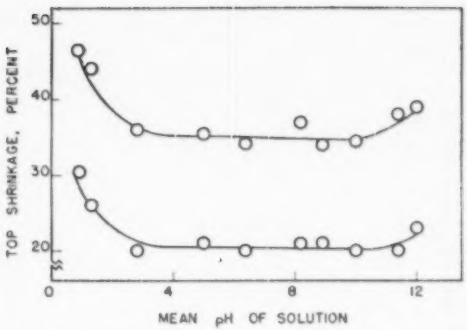

Fig. 6. *The effect of pH of the medium on top shrinkage.* Upper curve—*10 min. of tumbling.* Lower curve—*4 min. of tumbling.*

Effect of Variation of Temperature

The effect of temperature on the top shrinkage value of untreated wool in several solutions is shown in Table I. Although the apparatus in its present form is not well adapted to experimentation at controlled elevated temperatures, the data reveal the expected increase in rate of felting with increasing mean temperature of the medium. The results are in agreement with those of Mercer on yarns [4] in that no critical felting temperature is observed in this range.

More important from the point of view of a control method is that the wool top treated for shrink-resistance does not appear to be very sensitive to temperature variation in the range 18°C to 33°C. Thus, a mildly chlorinated wool top giving 21% top shrinkage by the standard test at 25°C gave similar results at 18°C and at 33°C. In terms of mill use, therefore, no special precautions are required for maintaining constant temperature for this test.

Effect of Weight of Sliver

The effect of varying the weight of the sliver on the results obtained in the top shrinkage test is

TABLE II. Effect of Weight of Sliver on Top Shrinkage in "Standard" Test

Weight of sliver (g./m.)	(oz./5 yds.)*	Top shrinkage value (%)
12.1	2.0	11
18.7	3.0	15
25.9	4.2	16
34.5	5.6	13

* The weight of a sliver is commonly designated in American mills as the number of ounces per 5-yd. length.

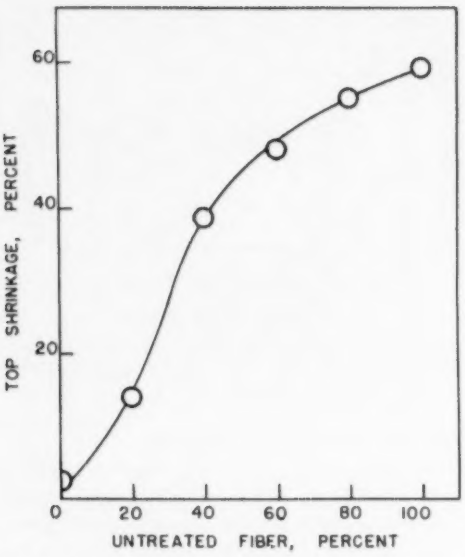

FIG. 7. *Effect of untreated fibers on the shrinkage of overtreated top.*

shown in Table II. These data are for slivers which span the usual commercial range for wool top. The results, which in this instance are for shrink-resistant tops gilled to various weights, indicate that the test is substantially independent of weight of sliver in the range tested.

It follows from the above result that the top shrinkage test should not be very sensitive to the number of slivers tested, at least within narrow limits. Since the number chosen (five) is convenient to use, provides a reasonable number of replicates, and does not overfill the apparatus, it has been used consistently.

Effect of pH

The effect of pH on felting in the top shrinkage test is shown in Figure 6. As shown by these results, the feltability of wool under these conditions is markedly greater in the acid region, does not change greatly in the pH range 4–10, and increases again in the more alkaline region. These experiments were performed in Clark and Lubs buffers [1] in the pH range 1–10, and with 0.1*N* NaOH (adjusted as required with H_3BO_3) for the more alkaline conditions.

A detailed discussion of this functional relationship between felting and pH of the medium is outside the scope of this paper. In passing, however, it is interesting to note the similarity between the curves in Figure 6 and that presented by Speakman *et al.* [6] relating the scaliness of keratinous fibers, as measured with the lepidometer, to the pH of various buffers.

For the purpose of a control method, the use of a dilute solution of sodium bisulfite as a felting medium is quite satisfactory. It buffers in the region in which the felting rate is insensitive to pH, and its common use in the mill as an antichlor makes it particularly convenient. It has therefore been used in the "standard" test, although many other buffering agents are equally satisfactory.

Top Shrinkage of Blends of Treated and Untreated Wool

It is generally recognized that the effectiveness of a chemical method in producing shrink-resistant wool depends in part upon its ability to treat the fibers to a uniform degree, and dyeing tests have often been used to evaluate the uniformity of treatment. The top shrinkage test offers a direct means for demonstrating the remarkable effect on felting of even a minor proportion of untreated fibers. For this purpose, samples of untreated wool and severely overtreated wool were gilled together to form homogeneous blends of varying proportions, and the blended slivers were then subjected to the top shrinkage test. The results of the measurements, which are shown in Figure 7, illustrate the important effect of the untreated fibers on the felting of the blend. Thus, 20% of untreated wool in a blend caused a substantial increase in felting, while 40% of untreated fibers resulted in a sliver that behaved more like untreated wool than like treated wool.

Correlation of Results of Top Shrinkage Test with Laundering Shrinkage

Over a period of approximately two years, the top shrinkage test has proved to be a useful tool for predicting the shrinkage that occurs during the laundering of garments fabricated from the treated top. Of course it must be recognized that the structure of the fabric (twist of yarn, knitting stiffness, type of knit, etc.) plays an important role in the shrinkage during laundering, as has been clearly shown by the

work of Dutton [2, 3]. The effect of construction must therefore be considered in making a fabric with a desired degree of shrink-resistance. For any given construction, however, the degree of treatment can be controlled and the laundering shrinkage predicted by means of the top shrinkage test. The close correlation between the results of this test and shrinkage of garments and fabrics after laundering in a wash wheel is shown in Table III. The results are representative for materials of typical commercial constructions; numerous similar correlations have been obtained with a variety of fabrics, and in the period it has been used the test has proved to be a reliable index of degree of shrink-resistance of a fabric during laundering.

Use of the Top Shrinkage Test as a Tool for Fundamental Studies

While the top shrinkage test was developed as a simple tool for control of processing, it appears to offer promise as a method for the study of the fundamentals of felting. Thus, it provides a rapid means of evaluating the rate and extent of felting of different wools, or of a given wool in different media. A study of the relationships existing between the felting of wool in different media and wool's swelling and mechanical properties is now in progress and will be reported elsewhere. Typical results for samples of wool top which were tumbled in various mixtures of isopropanol and water are presented in Figure 8. As shown by this graph, the wool felts to a relatively great degree in water and to a smaller extent in isopropanol, which is a less polar solvent and a poorer swelling agent. The somewhat surprising maximum in the curve is perhaps analogous to the effect described by Speakman [5] on the elastic properties of wool in mixtures of various alcohols. The maximum is related to the swelling and mechanical properties in the mixture, as will be shown in a future publication.

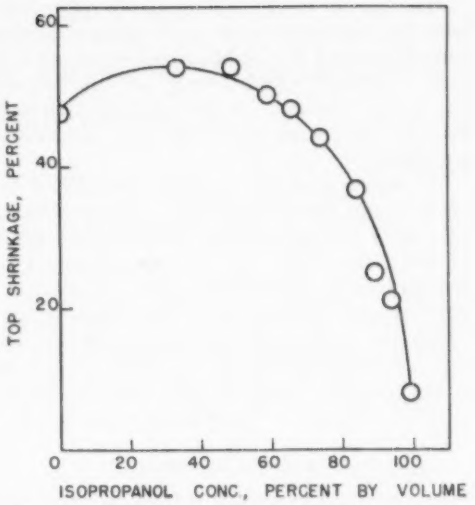

Fig. 8. *Shrinkage of untreated top in isopropanol-water solutions.*

TABLE III. Relationship Between Top Shrinkage Value and Laundering Shrinkage of Fabrics

Sample	Top shrinkage value (%)	Felting (length) shrinkage after 10 launderings (%)
Flat knit socks	1 (Severe treatment)	1
	9	4
	15	5
	40 (Untreated control)	18
Rib knit socks	1 (Severe treatment)	2
	9	6
	15	9
	40 (Untreated control)	21
Sweaters	17 (Mild treatment)	−2
	23	10
	30	12
	47 (Untreated control)	23
Worsted flannel	10 (Severe treatment)	1
	45 (Untreated control)	15

TABLE IV. Effect of the Nature of the Medium on the Felting of Wool Top

Reagent	Top shrinkage value (%)	Time of tumbling (min.)
0.2*M* $CaCl_2$	32	10
0.5*M* $CaCl_2$	29	10
1.0*M* $CaCl_2$	24	10
3.0*M* $CaCl_2$	13	10
1.8% HCOOH	38	4
9% HCOOH	43	4
20% HCOOH	45	4
H_2O	47	10
H_2O	29	4

The effects of typical swelling and deswelling systems (aqueous solutions of formic acid and calcium chloride, respectively) on the felting of top are indicated in Table IV. These results, and their relationship to the mechanical properties of the wool fiber, will also be discussed in detail in a forthcoming publication.

The results given here show the usefulness of the top shrinkage test as a rapid and convenient method for control in distinguishing quantitatively between a wool sliver which has been treated to impart shrink-resistance and untreated wool. Its use eliminates the long time required for fabrication of fibers into a yarn or fabric, permitting immediate evaluation of the shrink-resistance of a sliver. A number of examples have also been given to illustrate the potential utility of the method as a research tool.

Acknowledgment

Grateful acknowledgment is made to the Barre Wool Combing Company, and particularly to Mr. John M. Gould and Mr. Richard Riley of that organization, for supplying the blended tops, slivers of various weights, and other samples described in this report.

The assistance of Ruth E. Smith, Virginia A. Giles, and Nancy J. Tucker in performing many of the laboratory measurements is thankfully acknowledged.

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Foreign-Matter Content in Bales of Cotton Used for Grade Standards

Dorothy Nickerson

United States Department of Agriculture, Production and Marketing Administration, Cotton Branch

In 1946 color measurements were reported [1] for the U. S. official standards for grade of American upland cotton. Except in official annual reports, there have been no reports made of the foreign matter in grade standards, or in cottons classed against those standards, although a scale based on such measurements is used for comparison of test results obtained with the Shirley Analyzer that are made as a part of our Cotton Testing Service [3, 6].

During the 1946 International Cotton Grade Standards Conference there was considerable discussion by manufacturers and others which indicated a widespread belief that the Government had increased the amount of trash in the 1946 standards for some or all of the grades. Since there had been no intention of making any change in the foreign-matter content of the grades, the color laboratory (after the conference) obtained samples of the standards bales in order to check on their foreign-matter content. Although it is the surface of the sample in the grade-standards boxes that represents the grade, nevertheless it was felt that a measurement and comparison of foreign matter in the bales would indicate whether there had been any inadvertent change in the standards between 1936 and 1946.

This report includes a study of the foreign-matter content of the bales used in preparing standards for the 1936 and 1946 International Cotton Grade Standards Conferences.

Method of Analysis

In order to supply a record of the foreign-matter content of cotton grade standards, it has been customary for many years to photograph each standards box after it is passed by the Review Committee and to place a full-scale copy of this photograph in the cover of each box. Photographs are compared for leaf with a photograph of the original or duplicate standard which is used as a guide in the preparation of boxes of similar grade. Although these photographs provide a record which can be checked, they do not make it easy to report a statistical measure of trash content, and measurements obtained with the Shirley Analyzer have therefore been used for trash analyses.

The Shirley Analyzer [2] is a laboratory instrument which was developed at the Shirley Institute, Manchester, England, which provides an effective means for making an almost complete separation of cotton lint and trash, with a minimum of fiber loss. After the separation the weight of lint fed into the machine, the weight of lint delivered, the weight of visible foreign matter, and the percentage of nonlint (calculated from the total of visible and invisible losses) are reported. Although the figures are based on weight determinations and although they do not take into consideration the nature of trash, which is sometimes as important as weight in determining grade, they are the best figures obtainable for providing a measure of trash content.

Nonlint removed by the Shirley Analyzer is distinguished from the total picker and card waste of the manufacturing processes by the fact that practically no fiber is included as it is in the usual waste from mill cleaning machines. Therefore, picker and card waste results reported on a basis of spinning tests are not expected to agree with results obtained with the Shirley Analyzer.

Procedure

In 1936 the cotton grade standards were revised. After approval of the grade standards by the delegates to the International Universal Cotton Standards Conference of 1936 [4], samples of each of the bales used in these standards were analyzed by means of the Shirley Analyzer. Immediately after the 1946 conference [5] similar analyses were made on bales used in preparing the 1946 standards in order to

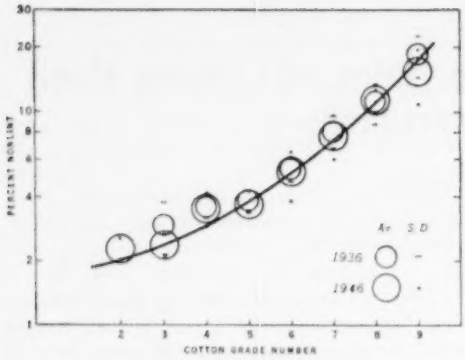

FIG. 1. *Average percent of nonlint in bales used for the 1936 and 1946 white grade standards.*

check on the agreement of 1946 standards bales with those of 1936.

Results

The agreement in percentage of trash content between the 1936 and 1946 standards bales for the same grades seems unusually good. Results are shown in Figure 1. The small circles represent 1936 averages of measurements for the bales in each grade; the bar represents the variation around this average, as measured by the standard deviation. The larger circles represent 1946 averages, and the dots represent the variation of trash content in individual bales of each grade. The relationship is not a straight line when plotted on a logarithmic scale, as was thought at first, but a smooth curve can be fitted to the data. Table I gives the nonlint contents for these two sets of standards bales and a grade conversion scale based on an average smoothed curve. For samples that are normal for color, leaf, and trash content, this conversion table can be used to give an equivalent-grade, based on measurements of trash content.

TABLE I. PERCENTAGE OF NONLINT* FOR BALES USED IN PREPARING COTTON GRADE STANDARDS

White grades No.	Percent nonlint: 1936 standards bales Av.	1936 standards bales S.D.	1946 standards bales Av.	1946 standards bales S.D.	From smoothed curve
2			2.26	±0.26	2.0
3	2.94	±0.83	2.38	±0.29	2.4
4	3.63	±0.44	3.51	±0.67	2.9
5	3.83	±0.45	3.69	±0.15	3.7
6	5.35	±0.73	5.12	±1.32	5.1
7	8.08	±1.37	7.71	±1.74	7.6
8	11.03	±2.25	11.25	±1.44	11.0
9	18.64	±4.13	15.17	±4.20	17.0

* Determinations made with the Shirley Analyzer.

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(*Manuscript received December 28, 1949.*)

Conference on Mechanical Properties of Plastics

June 19–21, 1950

Plastics and their mechanical properties as viewed from the standpoint of research, engineering, and architecture will be the subject of a three-day conference at the Massachusetts Institute of Technology on June 19, 20, and 21, 1950.

Sponsored by the M.I.T. Plastics Committee, the program will provide an opportunity for those interested in but not directly associated with plastics to hear and participate in discussions of their many properties and uses. Research workers in the field will report their findings for discussion by others engaged in research as well as by engineers involved in plastics applications.

Further information may be obtained from Prof. A. G. H. Dietz of the Department of Building Engineering and Construction, Massachusetts Institute of Technology.

The program is as follows:

Monday, June 19

Turner Alfrey, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.
"The Theory of Visco-Elastic Behavior of High Polymers"

E. Guth, University of Notre Dame, Notre Dame, Ind.
"Static and Dynamic Properties of Rubberlike Materials"

W. O. Baker, Bell Telephone Laboratories, Murray Hill, N. J.
"Reaction of Polymers and Mechanical Waves"

W. P. Mason, Bell Telephone Laboratories, Murray Hill, N. J.
"Mechanical Properties of Plastics at Ultrasonic Frequencies"

R. Buchdahl and Laurence E. Nielsen, Monsanto Chemical Company, Springfield, Mass.
"The Usefulness of Basic Mechanical Properties in the Evaluation of Plastic Materials"

R. D. Andrews, Princeton University, Princeton, N. J.
"Mechanical Properties of Linear Amorphous Polymers"

Tuesday, June 20

Waller George and George Irwin, Naval Research Laboratory, Washington, D. C.
"Flow Markings in Polymeric Solids"

R. S. Spencer, Dow Chemical Company, Midland, Mich.
"Injection Molding of Polystyrene"

I. L. Hopkins, Bell Telephone Laboratories, Murray Hill, N. J.
"Complex Stressing of Polymers"

J. A. Kies, Naval Research Laboratory, Washington, D. C.
"Origin and Interpretation of Fracture Markings in Plastic Materials"

W. J. Gailus, Massachusetts Institute of Technology, Cambridge, Mass.
"Flow and Fracture Characteristics of Polymethyl Methacrylate"

Steven Yurenka, Massachusetts Institute of Technology, Cambridge, Mass.
"Creep and Relaxation Properties of Polymethyl Methacrylate"

Earl Patterson, Massachusetts Institute of Technology, Cambridge, Mass.
"The Effect of Molecular Weight Distribution on the Stress-Strain Properties of Polymethyl Methacrylate"

R. G. Cheatham, Massachusetts Institute of Technology, Cambridge, Mass.
"The Effect of Orientation of Molecules on the Mechanical Properties of Polystyrene"

Wednesday, June 21

Robert Burns, Bell Telephone Laboratories, Murray Hill, N. J.
"Mechanical Properties of Rigid Plastics"
R. H. Carey, Bakelite Division, Union Carbide and Carbon Corporation, Bound Brook, N. J.
"Evaluating Mechanical Properties of Polyethylene and Other Nonrigid Plastics"
George H. Clark, The Formica Company, Cincinnati, Ohio
"Plastics-Based Laminates"
F. M. Reinhart, National Bureau of Standards, Washington, D. C.
"Engineering Adhesives"
M. R. Euverard, Interchemical Corporation, Newark, N. J.
"Protective and Decorative Industrial Finishes"
N. J. Rakas, National Automotive Fibers, Inc., Detroit, Mich.
"Synthetic Textiles in Automobiles"
L. Boor, Philadelphia Quartermaster Depot, U. S. Army
"Films and Coated Fabrics"
G. M. Kline, National Bureau of Standards, Washington, D. C.
"Resistance of Plastics to Various Service Conditions"

"Detection of 'Honeydew' on Raw Cotton"

Of interest to users of raw cotton will be a pamphlet issued by the U.S.D.A. Southern Regional Research Laboratory which describes a reliable confirmatory test for the presence of a sticky or gummy substance called "honeydew," which frequently makes the cotton difficult to process in the mill.

Honeydew may occur on cotton grown in any area provided the conditions are favorable to the heavy infestation of aphids at the time the cotton bolls are open. This contamination has caused some difficulty on Western, irrigated-grown cottons from the 1949 crop.

This report, "Detection of 'Honeydew' on Raw Cotton," published in February, 1950, may be obtained without charge from the Southern Regional Research Laboratory, New Orleans.

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